

Photoelectron spectroscopy within a correlated one-particle picture

Bibek Samal, Vamsee K. Voora

Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

Email: bibek.samal@tifr.res.in

X-ray photoelectron spectroscopy (XPS) provides valuable information about the local chemical environment of atoms in molecules by directly probing core electron binding energies (CEBEs). XPS technique is now increasingly used to investigate complex chemical systems thanks to the advent of high-brilliance X-ray sources. To complement these advances we recently proposed a scalar-relativistic (SR) GKS-spRPA method that helps to model X-ray emission spectra of small to medium sized molecules within a one-particle framework. SR-GKS-spRPA is a robust theoretical technique that avoids variational collapse issues and provides accurate core-hole state based X-ray emission. We now extend the SR-GKS-spRPA technique to incorporate spin-orbital coupling (SOC) effects which are necessary to understand L-edge XPS. The new algorithm incorporates SOC perturbatively in the exact two-component (X2C) framework, the perturbative SOC corrections are computationally cheap compared to the SR analogue. We use the SOC-GKS-spRPA to model K-edge and L-edge XPS of molecules containing third-period elements and analyse its accuracy.

References:

1. V. K. Voora; R. Galhenage; J. C. Hemminger; F. Furche. Effective one-particle energies from generalized kohn–sham random phase approximation: A direct approach for computing and analyzing core ionization energies. *J. Chem. Phys.*, 2019, 151(13), 134106.
2. Y. J. Franzke; N. Middendorf; F. Weigend. Efficient implementation of one- and two-component analytical energy gradients in exact two-component theory. *J. Chem. Phys.*, 2018, 148, 104110,.
3. B. Samal, V. K. Voora,; Modeling Nonresonant X-ray Emission of Second- and Third-Period Elements without Core-Hole Reference States and Empirical Parameters; *J. Chem. Theory Comput.* 2022, 18, 12, 7272