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A Parameter-Free Approach for Modeling Valence and Core-Level Photoelectron Spectroscopy

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Core-level spectroscopy provides valuable information about the local chemical environment of atoms in molecules by probing core-electronic structure whereas valence-level spectroscopy offers valuable insight into hybridization and bonding via valence-electronic structure. Despite their similarity, modeling core-electronic structure is challenging owing to large orbital-relaxation effects and relativistic corrections. We overcome these challenges by combining the generalized Kohn–Sham semicanonical projected random phase approximation (GKS-spRPA) mehod with the spin-free exact two-component theory in its one-electron variant (SFX2C-1e) followed by a perturbative treatment of spin-orbit coupling (SOC) to model the K- and L-edge X-ray photoelectron spectroscopy (XPS), valence-level PES and non-resonant X-ray emission spectroscopy (XES) of molecular systems. The core and valence-electron one-particle states, required for the computation of the XES spectra, are obtained directly in a single calculation of the neutral system without any use of core-hole reference states. A comprehensive analysis demonstrates that the X2C-GKS-spRPA method achieves an accuracy of approximately 0.2 eV for valence-level PES and XES, while mean absolute errors (MAEs) of less than 1 eV are observed for core K-edge and L-edge XPS of third-period elements. We also show that an analytic continuation technique, with a O(N4) computational cost, can be used to obtain highly accurate X-ray emission spectra of molecules such as C60 and S8 with multiple core-hole states.

Abstract category

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