Using density functional theory to reveal many-body contributions to X-ray excited states

David Prendergast[1]

[1]*The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, USA*

X-ray spectroscopy can provide valuable insight into materials phenomena, especially at or near interfaces. Nominally, measured spectra provide projections of the electronic density of states with chemical specificity. X-ray excitations, particularly when resonant, generate significant electronic structure perturbations, which may prove challenging, in certain cases, for linear-response theories, particularly if they involve multiple electron-hole pair excitations. For the purposes of more accurately modeling X-ray spectra and excited-state electronic structure, we employ constrained density functional theory to directly approximate key X-ray final states around which we build spectral calculations. Within this final-state approach we include contributions from all occupied electronic orbitals, recognizing that strong polarization and charge transfer may accompany core-orbital excitations.[1,2] Recently, we have observed the strong prevalence of so-called shake-down processes in final-state approximations to core-excitations and their role in introducing spectral contributions from multiple electron configurations accessible to the final state. The purpose of this theoretical approach is to reveal the origins of various spectral details and to provide guidance to the design of future experiments.

Keywords: Theory, Simulation, Modeling, X-ray Spectroscopy

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