

Title: Calculations of core level spectroscopies including many-body effects: influence of the model

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Core level spectroscopies are precious tools to obtain insight about the electronic structure of materials. To support the interpretation of experiments, numerical simulations are often needed. When the final state is localized and electronic repulsions are strong (for example, for the $L_{2,3}$ edges of transition metals or $M_{4,5}$ edges of rare earth elements), multielectronic effects must be included in the calculation. To describe these spectra, multiplet ligand-field (MLF) calculations are a method of choice because they include all Coulomb interactions and multiplets within a cluster around the absorbing atom. Traditionally, MLF calculations are parameterized which make it a semi-empirical method. For some time now efforts have been made to compute the needed parameters from first principles. A description of the lower energy bands of the crystal with Wannier orbitals is, for example, a way to obtain almost all of the needed parameters from a band structure calculation.¹

*Quanty*² is quantum many body tool which makes possible to perform MLF calculations of a large diversity of spectroscopies: X-ray absorption (XAS), $2p$ and $1s$ core-level photoemission, non resonant inelastic X-ray scattering (NRIXS) at the $M_{2,3}$ -edges (including $3p$ to $3d$ octupole transitions for large momentum transfer), NRIXS of the $d-d$ excitations, optical spectra... Thanks to recent developments to include the Auger decay, the core-hole lifetime can be computed *ab-initio*. We used *Quanty* in association with FPLO which is a Kohn-Sham density functional theory (DFT) implementation based on local orbitals and a full-potential.³ The combination of the two codes provides a very flexible method to compute core level spectra including multiplet effects with a minimal number of parameters. The description of the ground state and of the excited states of a material can be based on many different models depending on the needed level of theory.

We will present the results obtained on the case of three strongly correlated Ni-based materials: NiO, NiS₂ and NiSe₂. Two of them, NiO and NiS₂, are antiferromagnetic insulators while NiSe₂ is a paramagnetic metal. We will compare different ways of describing the ground state of these materials: from simple paramagnetic DFT calculations, which are able to reproduce the crystal structures but not the insulator character of NiO and NiS₂, to cluster dynamical mean-field theory which includes on-site correlations. For various spectroscopies, we will compare the calculated spectra with experimental spectra.

These calculations are important to understand the impact of the correlations on the core level spectroscopies. We will discuss in detail which level of theory is needed to describe the spectra depending on the technique and on the edge of interest. We will also comment on the importance of spin-orbit coupling and of electron-phonon coupling.

REFERENCES

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