

Transition metal L-edge spectra with ligand-field multiplet parameters from density functional theory

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Introduction.

Transition metal L23-edge absorption spectra provide rich information on the electronic and magnetic state of metal sites in complex matter. The ligand field multiplet (LFM) model is the most widespread and successful method for their theoretical description. In the LFM model, the perturbation of the 3d atomic shell by the ligands is described through empirical parameters, namely the ligand field splittings and Coulomb integral reduction factor. For complex systems, with inequivalent metal sites of low symmetry, the number of fitting parameters becomes too large for a meaningful analysis.

Theoretical methods.

We have developed a simple method for computing all parameters of the LFM model, for arbitrary symmetry, from the electronic ground state of the system as obtained in density functional theory. From integrals over symmetry projected density of states, we determine ligand field splittings and covalency parameters. The latter are used for rescaling the Coulomb integrals. We thus take account of the anisotropy of the Coulomb reduction factors for the first time within the LFM approach.

Results and discussion.

We apply the method to transition metal oxides and low symmetry metal-organic molecules and obtain excellent result in most cases. We find that the anisotropy of the Coulomb integrals has a small but non-negligible effect on the spectra and brings them to better agreement with experiment. When the metal-ligand bond has a strongly covalent character, the LFM model is insufficient and the ligand orbitals need to be included explicitly in the model through a charge transfer cluster approach. We propose a simple charge transfer model for any symmetry and extract the ligand dependent parameters (ligand levels and hybridization strengths) from density functional theory. We test the method for a number of metal-organic molecules with nitrogen and carbon bonds and obtain good agreement with experiment.

Conclusion.

We have developed a simple scheme for performing parameter-free L-edge absorption calculations within the ligand field multiplet and cluster model approach, where the model parameters are obtained from the density functional theory. Thereby L-edge spectra become predictable for complex systems and the relation to the ground state electronic structure of the entire system becomes apparent.