

# Transition metal L-edge spectra calculations with non-empirical parameters

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Ligand field multiplet (LFM) theory is the standard method for computing X-ray absorption spectra from transition metal L-edges [1]. In this one-ion model, all extra-atomic effects are described by a ligand field and a Coulomb integral reduction factor ( $\kappa$ ). Despite its simplicity, the LFM method is astonishingly successful, showing that it contains the relevant physics of the problem. The major drawback is that the parameter values (ligand field strengths and  $\kappa$ ) need to be fitted to experiment which makes the method non-predictive. This is especially problematic for complex systems with many inequivalent sites and/or low symmetry where the number of fitting parameters is large.

We have devised a simple method [2] for extracting all parameter values from the ground state electronic structure of the system, which can easily be computed using, e.g. density functional theory. Apart from ligand field strengths, we also compute the orbital dependent covalency, which lead to anisotropic Coulomb integral reduction factors. This anisotropy effect has been taken into account for the first time in LFM calculations. We apply the method to transition metal oxides and metal phthalocyanines, and obtain good agreement with experiment in all cases. In the case of low symmetry systems (phthalocyanine,  $V_2O_5$ ) the covalency factors are highly anisotropic and have a substantial influence on the spectra.

## References

- [1] F. M. F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids*, CRC Press, Boca Raton (2008).
- [2] P. Krüger, *Ab initio calculation of ligand field multiplet parameters for transition metal L-edge spectra*, *Radiat. Phys. Chem.* (2019) on-line. DOI: 10.1016/j.radphyschem.2018.11.005