Multiplet ligand field approach based on Wannier functions for ab initio simulations of RIXS

Guda Alexander (1), Gorelov Evgeny (2), Guda Sergey (3), Bugaev Aram (1, 4), Lamberti Carlo (1, 4, 5), Soldatov Alexander (1)
(1) The Smart Materials Research Center, Southern Federal University, Sladkova 178/24, 344090, Rostov-on-Don, Russia
(2) European XFEL GmbH, Holzkoppel 4, 22869 Schenefeld, Germany
(3) Institute of mathematics, mechanics and computer science, Southern Federal University, Milchakova 8a, 344090, Rostov-on-Don, Russia
(4) Department of Physics and NIS Interdepartmental Center, University of Torino, via Giuria 1, I-10125, Torino, Italy
(5) Department of Chemistry, INSTM Reference Center and CrisDi Interdepartmental Center for Crystallography, University of Torino, via Giuria 7, I-10125, Torino, Italy

guda@sfedu.ru

Advanced quantitative analysis of the local atomic geometry around active sites in metalorganic frameworks [1] requires novel experimental methods such as resonant valence to core XES, resonant inelastic scattering RIXS or the pre-edge structure of XANES measured in high energy resolved mode. However, there is no widely used ab initio theoretical method which could be routinely applied to the analysis of such experimental data except parametric multiplet calculations [2,3]. The way to overcome procedure of adjusting of parameters is the using of local DFT Hamiltonian constructed on the basis of wannier orbitals [4].

Resonant spectra were calculated using the QUANTY and XTLS codes in the framework of multiplet ligand-field theory using Wannier orbitals. In our calculations, we use material-specific model parameters obtained by means of a DFT and local cluster many-body model, including 3d orbitals + 4p orbitals with a full onsite Coulomb interaction and a metal local environment, treated as 10 composite ligand orbitals. Band structure calculations were performed by means of a full potential linearized augmented plane-wave approach, implemented in WIEN2k. The set of Wannier orbitals has been constructed based on the delocalized Bloch functions using an algorithm for construction of maximally localized wave functions within the Wien2wannier interface and the Wannier90 code.

The approach was tested on a set of reference compounds with different symmetry of 3d metal site and number of d-electrons. The structures under consideration were $CoCr_2O_4$, MnO, FeO, CoO, Fe2SiO4, $BaCoP_2O_7$, alpha-Fe_2O_3 and containing both octahedral and tetrahedral positions Fe_3O_4, Mn_2O_3. We show the potential interest of such ab initial calculations for the problem of gas adsorption on the active sites of metal-organic frameworks using CPO-27-Ni as a model system. We have constructed the hopping matrices for bare CPO-27-Ni and CPO-27-Ni with CO, NO, H_2O and H_2S adsorbates. The resulting resonance spectra are sensitive to the Ni-adsorbate distance and orientation of the molecule.

In conclusion we have implemented the 4p-3d hybridization in the framework of multiplet ligand-field theory using Wannier orbitals. This approach allows ab-initio simulations of resonance spectroscopic properties of various compounds even without symmetry. We show how such calculations can be used to determine distance and bending angle of the adsorbate molecule near active 3d metal center of metal organic frameworks.

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