Configuration interaction analysis for transition-metal oxides with negative charge-transfer energy

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Transition-metal compounds show surprisingly rich physical properties due to strongly correlated d electrons with spin, charge, and orbital degrees of freedom [1]. However, high valence transition-metal oxides and transition-metal chalcogenides have negative ligand-to-metal charge-transfer energy Δ_{CT}, and ligand holes are actively involved even in their ground state properties. Historically, the configuration interaction (CI) analysis of core level spectroscopy has been playing essential roles to identify the exotic electronic structure of negative Δ_{CT} materials. In addition to the classical systems such as $CaFeO_3$ [1], various transition-metal compounds with negative Δ_{CT} have been discovered. For example, the Ni site in Ta_2NiSe_5 has been found to have Δ_{CT} of -3 eV using CI cluster-model analysis on the Ni 2p core level, and the negative Δ_{CT} is associated with its exotic electronic state as an excitonic insulator [2]. On the other hand, the ligand holes in negative Δ_{CT} materials can be probed by x-ray absorption spectroscopy (XAS) of ligand core levels. For examples, oxygen holes in Li_xCoO_2 [3] and $Ba_3CuSb_2O_9$ [4] have been identified by combination of O 1s XAS and mean-field calculation. The agreement between theory and experiment can be improved by introducing CI to the mean field solutions. Such CI analysis is expected to describe new oxygen hole systems such as Li_2MnO_3 [5] and FeO_2 [6] in which oxygen-oxygen bonds play some roles to stabilize the oxygen holes in addition to the metal-oxygen bonds.

The authors would like to thank Prof. D. I. Khomskii, Prof. G. A. Sawatzky, Prof. A. Fujimori, Prof. M. Okubo, and Dr. Takubo for long term collaborations on the electronic structure of various transition-metal compounds.

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