Prediction of spin orientations in terms of HOMO-LUMO interactions using spin-orbit coupling as perturbation

A talk by M.-H. Whangbo

Department of Chemistry, North Carolina State University, USA

DATE / TIME: Monday, June 13th 2016, 4:00 p.m.

LOCATION: Erwin-Schrödinger Lecture Hall, 5th floor, Boltzmanngasse 5, 1090 Vienna

---

At a low temperature the spins of a magnetic solid may undergo a long-range magnetic ordering, which allows one to determine the directions and magnitudes of spin moments by neutron diffraction refinements. The preferred spin orientation of a magnetic ion can be predicted on the basis of DFT calculations including electron correlation and spin-orbit coupling (SOC). However, most chemists and physicists are unaware of how the observed and/or calculated spin orientations are related to the local electronic structures of the magnetic ions. This is also true even for most crystallographers who determine the directions and magnitudes of spin moments because the latter are treated merely as the parameters needed for the diffraction refinements. In this talk we will discuss a conceptual framework of thinking about and predicting the preferred spin orientation of a magnetic ion by examining the relationship between the spin orientation and the local electronic structure of the ion. In general, a magnetic ion M in a solid or a molecule is surrounded with main-group ligand atoms L to form an MLn polyhedron, and the d-states of MLn are split due to the interactions of the metal d-orbitals with the p orbitals of the surrounding ligands L. The magnetic ion M of MLn has a certain preferred spin direction, because its split d-states interact among themselves under SOC and because the strengths of these interactions depend on the spin orientation with respect to the coordinate system of the MLn. Within the LS coupling scheme, the preferred spin direction can be readily predicted on the basis of perturbation theory, in which the SOC is taken as perturbation and the split d-states as unperturbed states, by inspecting the magnetic quantum numbers of its d-orbitals present in the HOMO and LUMO of the MLn polyhedron. Implications of this observation concerning the spin-half syndrome and the spin-orbital entanglement of 5d magnetic ions will be discussed.