Multiplet splittings in organometallic compounds: a GGA+U approach

Damian Scherlis[1], Matteo Cococcioni[1], Patrick Sit[2], and Nicola Marzari[1]

[1]*Department of Materials Science and Engineering, MIT*
[2]*Department of Physics, MIT*
Cambridge, MA, USA

Iron enzymes and iron organic complexes have been extensively studied using first-principles quantum mechanical approaches in a variety of biophysical and chemical contexts. However, the application of quantum-mechanical methods is often limited by the deficiencies of conventional electronic structure techniques - such as Hartree-Fock or DFT - to provide even a qualitative description of the multiplet splittings for the transition-metal centers. We investigate here the GGA+U approach as a viable solution to describe the low-lying states of ligated and unligated iron heme complexes. Besides their central role in organometallic chemistry, they represent a paradigmatic case where LDA, GGA, and common hybrid DFT functionals fail to reproduce the experimental magnetic splittings. In particular, the imidazole pentacoordinated heme is incorrectly described as a triplet by LDA, GGA and B3LYP. We used a self-consistent linear-response formulation to calculate the Hubbard term U, and obtained spin transitions and molecular geometries in quantitative agreement with experiments. These results point to GGA+U as an appealing tool in the description of bioinorganic complexes, at a much reduced cost compared to correlated quantum-chemistry methods.