

Electronic Structure of Molecular Magnets: Successes within GGA and Challenges for SIC

Mark R. Pederson

Department of Chemistry, Johns Hopkins University, Baltimore MD, 21218

The experimental observation of resonant tunneling of magnetization in molecular magnets has led to significant theoretical interest in the first-principles electronic-structure based understanding of the magnetic- and spin-dependent- processes in these systems. For cases where the electronic structure is described qualitatively correctly, the PBE-GGA has been rather successful in accurately predicting many-of the molecular magnets composed of 3d-transition metal ions. Predictive successes include quantitative determination of magnetic reorientation barriers and the qualitatively correct description of the spin-excitation spectrum. This talk will highlight some of these successes[1,2] but focus on identifying challenging molecular-magnetic systems where the use of self-interaction corrected versions of density-functional theory is expected to lead to better predictive capabilities. For example for the Cu_3 and V_{15} molecular magnets, both of which simplify to a frustrated equilateral triangle of three spin $\frac{1}{2}$ transition-metal cations, the PBE-GGA provides the correct low-energy spin states but overestimates the splittings between the low-lying Kramer doublets and the upper quartet due to the slightly delocalized d-electrons on the transition-metal sites[1]. Rationale for why electronic-structure calculations with self-interaction-corrected functionals, could improve spin-excitations will be discussed. In regard to understanding spin-dependent electron transfer across molecular magnets, it is necessary to accurately calculate the charge states of a molecular magnet that is tethered to a distant electrode by a polymer. Through applications of DFT involving to Mn_{12} and Fe_4 molecular magnets as possible circuit elements and gold- and spin-polarized graphene flakes as possible substrates, the relation of the level alignment problem to the self-interaction correction will be highlighted. A new unitarily-invariant method for efficiently and exactly accounting for the self-interaction corrections for all electrons, with applications to simple transition-metal systems will be briefly introduced and discussed[3]. [1]MR Pederson and SN Khanna, Phys. Rev. B **60**, 9566 (1999), [2]J. F Nossa, MF Islam, CM Canali and MR Pederson, PRB **85** 085427 (2012). [3]M. R. Pederson, A. Ruzsinszky, and J. P. Perdew, J. Chem. Phys. **140**, 121103 (2014).