Calculations of Magnetic States of Transition Metal Clusters Using a Self-Interaction Corrected Energy Functional

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While Kohn-Sham density functional theory (KS-DFT) has been extremely successful and is now widely used in the studies of molecules and condensed matter it has several shortcomings. This is mainly due to the self-interaction error (SIE) inherent to practical implementations of the method. The Perdew-Zunger self-interaction correction (PZ-SIC) method is a way to correct for SIE [1]. Calculations based on PZ-SIC can describe challenging systems where conventional exchange-correlation functionals fail, such as defect states in crystals [2]. In this study PZ-SIC is applied in calculations of magnetic states of small iron clusters (see Figure below) and manganese dimer, and in both cases are shown to improve the agreement with experiments [3, 4] compared to KS-DFT. The experimental measurements indicate that Fe_{13} is anomalous, having antiferromagnetic ordering while the other Fe clusters are ferromagnetic. The reason for this is not known but could be related to the presence of impurities that destabilize the symmetric icosahedral structure. Experiments have shown that the Mn_2 dimer is antiferromagnetic, whereas PBE calculations predict a ferromagnetic ground state with magnetic moment 10 μ_B, and a bond length of 2.6 Å. PZ-SIC correctly predicts the antiferromagnetic state (0 μ_B), and a bond length of 3.3 Å which is in good agreement with the experimental value of 3.4 Å [5], and high-level, quantum chemistry calculations (3.1-3.6 Å) [6].

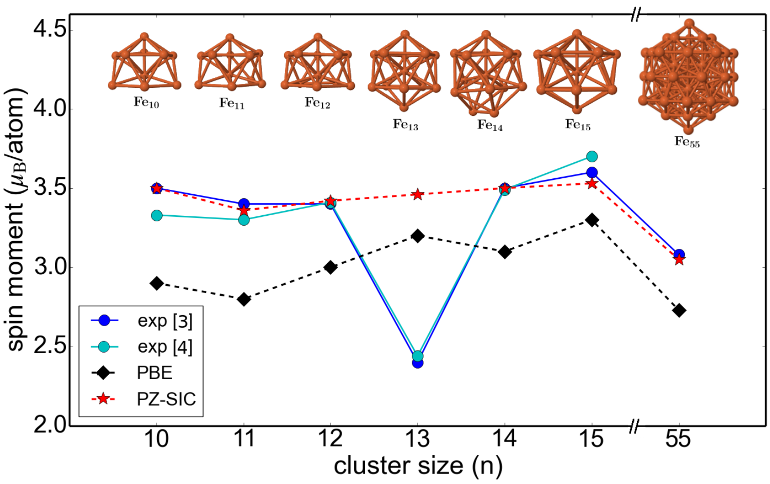

Fig. 1: Experimental and theoretical magnetic moment per atom in Fe_n clusters as a function of size, calculated with PBE and PZ–SIC applied to PBE. PZ–SIC improves upon the PBE results, and gives good agreement with the experimental results, except for Fe_{13} which is anomalous.

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