Prediction of Heisenberg Exchange constant in molecular magnetic wheel Mn$_{12}$(mda) complex using DFT+U

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Single-molecule magnets (SMM) are a class of polynuclear transition metal complexes, which are characterized by a large spin ground state and considerable negative anisotropy. These properties lead to a barrier for the reversal of magnetization. For these reasons SMM are expected to be promising materials for molecular spintronics and quantum computing applications. The idea of using SMM to implement the idea of quantum computer was proposed by Leuenberger and Loss. Instead of the classical bits, which can take only one value (1 or 0), quantum computers operate with quantum bits (qubits, prepared in quantum superposition state of 1 and 0) and carry out multiple operations at the same time. The electron spin is a natural candidate for a qubit, as its interaction with the environment is weaker than for the charge state. To choose superior candidate for quantum computation, we need to predict the differences of energies, between parallel (ferromagnetic) and antiparallel spin orientations (antiferromagnetic) of the transition metal centers in the molecules. This energy gap represented by a parameter called, Heisenberg exchange coupling constant (J). Long decoherence time is critically important for the successful realization of the quantum computer. A specific type of molecular magnets, called antiferromagnetic molecular wheels attracted especial attention for this reason, inside this wheel different antiferromagnetic and ferromagnetic interactions are present. For a suitable candidate for quantum computation qualitative and quantitative comparison for different J values inside this wheel is needed. Predictions of magnetic coupling in these systems have posed a long standing problem, as calculations of this kind require a balanced description of static and dynamic electron correlation. The large size of these systems limits the choice of theoretical methods used. Two methods feasible to predict the exchange coupling parameters are broken symmetry Density Functional Theory (BSDFT) and DFT with empirical Hubbard U parameter (DFT+U). In this contribution we report DFT+U to study Mn$_{12}$(mda) wheel using Vanderbilt Ultrasoft Pseudopotential plane wave DFT method, implemented in Quantum ESPRESSO code. Unlike most previous studies, we adjust U parameters for both metal and coordinated ligand atoms using five bineuclear manganese complexes as the benchmarks. For this work the we select a representative set of five different classes, based on the oxidation number and type of bridging groups: (i) Mn(IV) di-μ-oxo; (ii) Mn(IV) di-μ-oxo-μ-carboxylato; (iii) Mn(III) μ-oxo-di-μ-carboxylato, (iv) Mn(III)Mn(IV) μ-oxo-di-μ-carboxylato and (v) Mn(II) tri-μ-carboxylato bridged systems. The bimetallic manganese complexes of these types have rich redox chemistry and play a functional role in a variety of biologically important metalloproteins. BSDFT could not correctly predict J for second third and fourth complex, whereas DFT+U was successful for all five complexes. In addition we successfully applied DFT+U for two other iron homovalent and chromium homoalent, and chromium iron containing heterovalent heteronuclear complexes. Next, we apply this methodology to Mn$_{12}$ molecular wheel. The weak antiferromagnetic coupling between two halves of the wheel made possible the experimental observation of the quantum superposition involving entangled magnetic states, which was reported for this system. Along with we also predicted ferromagnetic interactions inside the wheel Unlike the published BSDFT study we treated whole molecule and calculate J between two halves of the wheel. Our study finds antiparallel spin alignment in weakly interacting fragments of Mn$_{12}$, in agreement with experimental observations.