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Exchange parameters in Fe-based molecular magnets

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Abstract

The calculation of interatomic magnetic exchange interactions entering the Heisenberg model is outlined from the standpoint of the density functional theory (DFT) for two Fe-based molecular magnets: a trinuclear complex with a Schiff base ligand, which is an antiferromagnetically coupled frustrated system, and a model bipyrimidine-connected planar network of Fe ions. First-principles electronic structure calculations are performed using the real-space method SIESTA and the full-potential linearized augmented plane wave FLAPW method FLEUR, correspondingly. We discuss the application of fixed spin moment technique for preparing the system in a given magnetic configuration, and the effect of intraatomic Coulomb correlation, approximated by the LDA + U technique, on the values of interaction parameters.

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1. Introduction

Since the first systematizations of their chemistry and basic properties by, e.g., Kahn in 1993 [1], molecular magnets are now developing into a promising class of magnetic nanomaterials with a great potential in applications in areas such as magnetic storage, quantum computing, or magneto-optical devices. An up-to-date review on microscopic properties (spin density, exchange interactions, magnetic anisotropy) of molecular magnets accessible in experiment and from first-principles calculations, is going to appear in Ref. [2]. Its major part is summarized as an internet publication [3]. In the present work we address the issue of extracting the interatomic exchange interaction parameters entering the Heisenberg model form the density functional theory (DFT). We discuss two chemical systems of different complexity. The actual calculations are done by two different methods, SIESTA [4] using compact and strictly confined atom-centered basis functions (see Ref. [5] for details), and the FLEUR [6] code, a realization of the highly accurate full-potential linearized augmented plane wave (FLAPW) method. Both calculations used the generalized gradient approximation after Perdew et al. [7] to the exchange-correlation functionals.

We skip the subtleties in the formulation of exchange parameters within the DFT; a detailed discussion can be found in Ref. [3]. Basically, we refer to total energies in different specially prepared magnetic configurations, calculated from first principles. Section 2 covers the extraction of meaningful results for a Fe-trinuclear system by applying the fixed spin moment formalism. Section 3 addresses a model Fe-binuclear system and, specifically, the importance of intraatomic correlation, treated beyond the conventional DFT formalism.

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2. Fixed spin moment treatment of a Fe-trinuclear system

One of the ways to arrive at the values of interaction parameters in a magnetic system whose properties are well described by the Heisenberg model is to compare total energies for different magnetic configurations. This is rather straightforward if, say, ferromagnetic (FM) and antiferromagnetic (AFM) states are well defined and at least metastable. A frustrated system, e.g., that with three antiferromagnetically coupled Fe atoms incorporated into an organic molecule, is a more complicated case. We consider specifically $Fe_3(OAc)_3L_3$, a synthesized by Boskovic et al. [8] derivate of the Schiff base H_2L = salicylidene-2-ethanolamine. The molecular unit used in the electronic structure calculation by the SIESTA method is shown in Fig. 2(a) of Ref. [8]. The magnetization measurements reported in Ref. [8] indicate an (almost AFM) ground state with the total spin $S = 1/2$, coming about from the interaction of three $s = 5/2$ spins of Fe(III) ions. Experimentally, the interaction parameters J of the Heisenberg model, introduced in Ref. [8] as $H = -2\sum_{\text{Fe pairs}} J_{ij}\mathbf{s}_i\mathbf{s}_j$, were reported to be necessarily different for an acceptable fitting of data, even as the molecule nearly maintains a trifold symmetry axis: $J_{ij} = -15.1$ K, -13.6 K, and -12.4 K.

We proposed earlier [9] to use the Fixed Spin Moment (FSM) method [10] for selecting a magnetic configuration of a molecular magnet (a six-center “ferric wheel”), improving simultaneously the stability of the electronic structure calculation. For the present system this idea becomes even more important, because it is not anymore obvious how to simulate a (nearly) AFM trial magnetic configuration in the DFT run, nor how to enforce an inversion of a selected local magnetic moment. On the contrary, by running a sequence of FSM calculations from the maximal nominal value of the total spin $S = 15/2$ (and higher) down to zero, one can scan the variety of all possible magnetic solutions within the DFT.

The results of our FSM calculation are shown in Fig. 1.[1] The total energy (left panel) has several local minima, the lowest one being for the FSM value of $5\mu_B$. From the right panel, in which local magnetic moments at three Fe centers are represented by three different symbols, one concludes that the case FSM = $5\mu_B$ corresponds to two Fe magnetic moments aligned in parallel and the third one aligned in the opposite direction. A competitive energy minimum is found for FSM = $15\mu_B$, i.e., the ferromagnetic configuration. The solution with FSM = $1\mu_B$ has higher energy than the latter one by 74 meV, per Fe atom. It should be noted that, whereas the ground state of the system is experimentally found to have $S = 1/2$, it must have a mixed nature over many quantum states, and hence does not correspond to any single-determinant DFT result. Nevertheless, the tendency for antiparallel coupling of Fe magnetic moments is correctly provided by our calculation; moreover the order of magnitude of the interaction constants can be correctly recovered: consistently with the above formula for the Heisenberg Hamiltonian, $-J \approx (E^{\uparrow\uparrow\uparrow} - E^{\uparrow\uparrow\downarrow})/(8s^2)$ amounts to 57 K. The error (overestimation by a factor of about 4) in the DFT calculation is nearly the same as we found earlier for the “ferric wheel” [9]. A possible reason for such systematic discrepancy can be the underestimation of the intraatomic Coulomb correlation, to be discussed in the next section.

Two issues might need further discussion. The HOMO–LUMO gaps shown in the middle panel of Fig. 1 are different in the FSM formalism for two spin directions, because the fixing of the total spin amounts to an imposition of an external magnetic field, moving apart the chemical potentials in two spin channels. Normally this would require the consideration of a Zeeman term when dealing with total energies. However, for a system with a *common* band gap in both spin channels a unique chemical potential can be found for both spin directions, therefore the FSM scheme would simply fix one or another of the metastable magnetic configurations at no additional energy cost. One can see that, indeed, a common band gap can be found in all situations relevant for our discussion, i.e. with FSM = 1, 5, and $15\mu_B$, thus justifying the extraction of the J value above. Another observation concerns the local magnetic moments at Fe sites: as the FSM value is changing, and even as the saturation of magnetization (at FSM = $15\mu_B$) is achieved, the local Fe magnetic moments merely flip, essentially maintaining their magnitudes of $4\mu_B$, and *not* $5\mu_B$. The nominal value of $s = 5/2$, associated with a single Fe atom, comes about due to magnetic polarization of ligands. This situation is identical to that described earlier for “ferric wheels” [3,9,11]. In spite of the very different structure of organic ligands, both systems have similarities in the nearest neighbourhood and in the charge state of Fe atoms (O_6 twisted octahedral coordination in “ferric wheels” vs. slightly distorted octahedral O_5N coordination in the present system).

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[1] It should be explained that the Fe-trinuclear complex reported in Ref. [8] crystallizes with two molecular units per primitive cell, which are slightly different. In particular, there is a formal disproportionality in the nominal electron number per these two fragments. As a consequence, a single molecular unit we took for our calculation possesses an odd number of electrons. Therefore only odd FSM values correspond to integer number of electrons in both majority- and minority-spin channels and may lead to an appearance of HOMO–LUMO gaps, shown in the middle panel of Fig. 1. However, even FSM values can be formally applied in the calculation as well, even as they possess no HOMO–LUMO gaps, because we applied an artificial broadening of molecular orbitals' eigenvalues (by 400 K). Some of such FSM numbers allow an easily converging calculation, with the total energy and local moments which follow the general trend. Such results are added in the left and right panels of Fig. 1.