



Preliminary communication / Communication

Molecular magnets explored by density functional theory calculations

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Received 2 March 2006; accepted after revision 10 July 2006

Available online 15 December 2006

Abstract

After a short introduction in the field of molecular magnetism, we focus on calculations of the magnetic anisotropy energy based on density functional theory. The results obtained make one confident in the predictive power of the formalism. **To cite this article:** *Jens Kortus, C. R. Chimie 10 (2007).*

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Keywords: Molecular magnetism; Nanomagnets; DFT magnetic anisotropy

1. Introduction

“Molecular magnetism deals with magnetic properties of isolated molecules and/or assemblies of molecules” [1], as expressed by Olivier Kahn, one of the founders of this research topic. This definition is quite general and there has been recently more emphasis on the aspect of the rational design of molecular magnetic properties in the field [2]. Therefore, molecular magnetism is seen “as a discipline which conceives, realizes, studies, and uses new molecular materials bearing new but predictable magnetic (and other) physical property” [3]. Research in molecular magnetism is driven by inter-disciplinary interaction between various fields in chemistry, physics, engineering and even biology.

This field of research is very attractive for first-principles microscopic simulations, because the crystal structure of molecular magnets is well defined,

reproducible and is made available rapidly. The progress in the field is clearly driven by advances in chemical synthesis of the materials and ingenious experiments. However, the combined efforts of physicists and material scientists, particularly theorists, inspire confidence that theory may become one day useful not only for explaining and prediction, but also for guiding the synthesis of new promising materials. As for now, the theory dealing with first-principles calculations tries to keep pace with experiment, still trying to reproduce it rather than to lead.

Nevertheless, there has been a notable progress in the prediction of exchange interactions and magnetic anisotropy energies from density functional theory during the last few years. The calculation of exchange couplings seems nowadays possible and feasible even for larger systems using methods based on density functional theory (DFT). For a recent review on the topic of calculation of exchange couplings using DFT see e.g. [4]. In contrast to cases where magnetic exchange interactions follow the famous Goodenough–Kanamori

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rules [5–7], we still have to await similarly clean general insights derived from theory in the case of magnetic anisotropy, which is another crucial property of molecular magnets, which could revolutionize the rational design of molecular nanomagnets.

2. Mn₁₂-acetate: the most famous example

The discovery of the molecule Mn₁₂O₁₂(CH₃-COO)₁₆(H₂O)₄ with a magnetic ground state of $S = 10$ showing a magnetic hysteresis [8] due to the properties of the single Mn₁₂-molecule has created large interest in the field. The observed hysteresis in molecular magnets is *not* due to re-orientation of domains as in conventional ferromagnets. Instead, it is an intrinsic molecular property that results from the magneto-crystalline anisotropy. This process can only be observed because the relaxation time is very large compared to the measurement time. The relaxation of the magnetization becomes indeed very slow at low temperatures (of the order of several months at 2 K). Therefore, by applying a magnetic field the material can be magnetized and will keep this magnetization for a long time if kept at very low temperatures. The so-called single-molecule magnets (SMM), which are also called molecular nanomagnets, can often be crystallized and form molecular crystals with relatively large distance between the molecular constituents. Therefore interactions between the molecular entities remain weak, so that the magnetic behavior probed by experiments is often dominated by intra-molecular effects.

Mn₁₂-ac has been synthesized and reported first in 1980 [9]. The molecular crystal has tetragonal symmetry with space group $I\bar{4}$, a single Mn₁₂-acetate cluster in the crystal poses an S_4 symmetry. There are now several modifications of Mn₁₂-acetate known, with different crystal structures, solvent molecules and water coordination — see Ref. [10] for more information.

3. Spin-orbit coupling and magnetic anisotropy energy

Strong spin-orbit coupling would try to align the spins of electrons in the magnetic d shell with the magnetic field. In a chemical environment, the d shell experiences a crystal field splitting due to the electric field of the neighboring atoms. The energy cost or gain of aligning the electron spins in an external magnetic field will then depend on the spatial arrangement of the d shell. In two special cases, however, the

magnetic anisotropy can be suppressed. If the crystal field splitting (i.e. anisotropic interaction with the ligands) is small, the spins in the d shell may freely rotate and will follow the external magnetic field, without much loss in energy. On the other hand, if the crystal field splitting is much larger than the spin-orbit coupling, the system (transition metal ion + ligands) prefers a configuration with zero (quenched) orbital moment and no magnetic anisotropy. In a semi-classical picture this orbital quenching can be interpreted, that the orbital momentum processes in the crystal field, so that its magnitude remains unchanged but all its components average to zero. However, the spin-orbit coupling cannot be completely ignored and it will mix in states with non-zero orbital momentum. This is responsible for the deviation of the g -factor from the pure spin value of 2.

Therefore, the height of the magnetic anisotropy barrier emerges by a quite subtle interplay between the strength of the spin-orbit coupling and the interaction with the crystal field due to the ligands. The temperature up to which a magnetic device will retain its preferential magnetic orientation is therefore determined by the magnetic anisotropy, hence high anisotropy is one of major priorities in the design of useful SMM devices.

Recently, Pederson and Khanna [11,12] have developed a method for accounting for second-order anisotropy energies. This method relies on a simple albeit exact method for spin-orbit coupling and a second-order perturbative treatment of the spin Hamiltonian to determine the dependence of the total energy on spin projection. It makes use of the Cartesian representation of the spin-orbit term, which is exact and also is more adaptable for multi-center systems.

4. Magnetic anisotropy in single-molecule magnets

The spin Hamiltonian describing the magnetic anisotropy up to second order can be expressed as:

$$H = DS_z^2 + E(S_x^2 - S_y^2). \quad (1)$$

We distinguish between axial and transverse anisotropies, with their corresponding parameters D and E .

The values of the axial anisotropy D available from a number of experiments for different SMM, and for several SMM first-principle calculations carried out with the use of the NRLMOL code are summarized in Table 1. The NRLMOL program package developed

Table 1
Comparison of the calculated (DFT-NRLMOL) and experimental magnetic anisotropy parameter D for selected single-molecule magnets

Molecule	S	$D(K)$	
		Theory	Experiment
$Mn_{12}O_{12}(O_2CH)_{16}(H_2O)_4$	10	-0.56^a	-0.56^b
$[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6Br_6]^{2+}$	10	-0.53^c	-0.30^d
$[Mn_{10}O_4(2,2'-biphenoxide)_4Br_{12}]^{4-}$	13	-0.06^e	-0.05^f
$Co_4(CH_2C_5H_4N)_4(CH_3OH)_4AcL_4$	6	-0.64^g	-0.7 to -0.9^h
$Fe_4(OCH_2)_6(C_4H_9ON)_6$	5	-0.56^i	-0.57^j
$Mn_9O_{34}C_{32}N_3H_{35}$	17/2	-0.33	-0.36^l
$Ni_4O_{16}C_{16}H_{40}$	4	-0.385	-0.40^l
$Mn_4O_3Cl_4(O_2CCH_2CH_3)_3(NC_5H_5)_3$	9/2	-0.58^m	-0.72^n

^a [11,14]; ^b [15,16]; ^c [17]; ^d [18]; ^e [19]; ^f [20]; ^g [21];

^h [22]; ⁱ [30]; ^j [23]; ^l [24]; ^m [25]; ⁿ [26].

by Pederson et al. is an all-electron Gaussian-type orbital implementation of DFT [13].

In all the cases presented here the calculated spin ordering is in agreement with experiment. The calculated D parameters for Mn_{12} , Mn_{10} , Mn_9 , and the ferric star Fe_4 are in excellent agreement with experimental values. The only remarkable discrepancy is found for Fe_8 , a system which seems to pose complications for the DFT treatment. Apparently the DFT may be unable to predict the ground-state density accurately enough due to important electronic correlations beyond the mean-field treatment. Similar deviations between experiment and theory have been found for a series of monomers, where D is underestimated by about a factor of two [27].

The SMM listed in Table 1 are in general characterized by a high-spin ground state. However, a high spin state does not necessarily correlate with a high anisotropy barrier. The prefactor D is also very important. In order to increase the barrier one has to understand and control D , which will be the main goal of future research in this area. In all cases where the E parameter is not zero by symmetry it has been predicted with similar accuracy as D – see relevant references for details.

The results obtained make one confident in the predictive power of the formalism. A microscopic understanding (based on the electronic structure of SMM) of the magnetic anisotropy parameters seems to be crucial for the rational design of single-molecule magnets.

Acknowledgments

The author thanks and appreciates useful discussions with A. Postnikov, Mark R. Pederson, Roberta Sessoli,

Jürgen Schnack, Eliseo Ruiz, Carlo Massobrio, Marc Drillon and Stefan Blügel. This contribution is partially based on similar work in collaboration with A. V. Postnikov [28,29].

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