Ab initio SIMULATIONS OF Fe-BASED FERRIC WHEELS

A. V. Postnikov[1*], J. Kortus[2**], S. Blügel[3]

[1] Universität Osnabrück – Fachbereich Physik,
D-49069 Osnabrück, Germany

[2] Max-Planck Institut für Festkörperforschung,
Heisenbergstr. 1, D-70569 Stuttgart, Germany

[3] Institut fur Festkorperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany

Abstract: Based on first-principles density-functional theory calculations we investigate the electronic structure of hexanuclear "ferric wheels" $MFe_6[N(CH_2CH_2O)_3]_6Cl$ (M = Li, Na) in their antiferromagnetic ground state. The electronic structure is presented in form of spin- and site-resolved local densities of states. The latter clearly indicate that the magnetic moment is distributed over several sites. The local moment at the iron site is still the largest one with about 4 μ_B, thus indicating the valence state of iron to be closer to Fe(II) than to commonly accepted Fe(III). The local spin of $S = 5/2$ per iron site, following from magnetization measurements, is perfectly reproduced if one takes the moments on the neighbor atoms into account. The largest magnetic polarization is found on the apical oxygen atom, followed by nitrogen and bridging oxygens. These findings are confirmed by a map of spatial spin density. A further goal of the present study has been a comparative test of two different DFT implementations, SIESTA and NRLMOL. They yield a very good agreement down to small details in the electronic structure.

1. INTRODUCTION

There has been a remarkable increase in the number of studies on molecular magnets during the last decade which clearly is driven by the progress in the chemistry of such systems. Many different families of molecular magnetic systems composed of all possible transition-metal atoms in various combinations with stabilizing organic ligands have been synthesized, their crystal structure determined and their magnetic properties analyzed [1].

While there is a large amount of experimental data available, the theoretical description in terms of quantitative – and often also qualitative – understanding is missing in some cases, in others it stays behind the experimental progress. The traditional approach to describe these systems is based on model Hamiltonians ("exact" diagonalization within, e.g., Heisenberg model). One the other hand, with the advance in computer technology and the development in theoretical methods, most notably in density-functional theory (DFT) [2], first-principles calculations became feasible. Both approaches simplify real systems and are prone to certain shortcomings. The model Hamiltonians neglect the true chemical environment and bonding. All interactions are reduced to just few model parameters. One is dependent on experimental input in order to estimate these parameters, and the accuracy of quantitative predictions depends on the parameters chosen. Even more problematic, it is not a priori clear which interactions are important and

* Corresponding author: tel. +49-541-969-2377, fax: +49-541-969-2351; email: apostnik@uos.de

Permanent address: Institute of Metal Physics, 620219 Yekaterinburg, Russia

** tel. +49-711-689-1664, fax:+49-711-689-1632; e-mail: j.kortus@ fkf.mpg.de

should be included in the model and which are negligible. In contrast, first-principles calculations based on quantum mechanics use the atomic positions as the only experimental input and, as chemical bonding is included in a straightforward way, they are able to provide microscopic foundations of the magnetic behavior. Unfortunately, the solution of Schrodinger's equation is limited to a few electrons so that one has to use approximations. The chemical complexity of molecular magnets (or, their large number of atoms) excluded so far the "straightforward" simulations using approaches of superior accuracy, like quantum Monte Carlo. Density-functional based calculations have become the working horse in today's first-principles simulations. DFT has been proven to be very accurate and reliable in many cases, although electron correlation effects beyond the mean-field approximation in DFT are neglected, which limits the accuracy and may lead to failures in the description of a given system.

Both approaches, the model-based and DFT-based, are useful and important for our understanding, and are best used together. While DFT can provide the input parameters for models (e.g. the exchange parameters J for a Heisenberg model), the model Hamiltonians can deliver information on many-body effects, temperature dependence, and quantum fluctuations, which are beyond the reach of DFT. By describing the relevant physics from different points of view one develops a complete picture where essential features do not remain unexplored.

Concentrating in the following on DFT-based strategies, we note that molecular magnets turn out to be hard cases for computational treatment – for different reasons in different established calculation approaches. The openness of the crystal structure creates problems for traditional muffin-tin- or atomic sphere approximation-based tools, and requires a "full-potential" formalism instead. The presence of transition metals and/or other constituents with deep semicore states, which can not be neglected, creates problems for pseudopotential planewave methods. Moreover, the need for a large (albeit largely empty) "simulation box" around a molecule makes planewave-related methods expensive. An abundance of hydrogen and hence strong disbalance in atom "sizes" makes the linearized augmented plane wave scheme numerically demanding. The often unusual chemical composition and coordination reduces the usefulness of *a priori* tuned basis sets in those tight-binding-type methods which heavily depend on pre-adjusted basis functions for their efficiency. Further, the option to treat non-collinear spin-density distribution and to have accurate forces on atoms for studying structure relaxation and dynamics may be advantageous and sometimes necessary. As a consequence, flexible, efficient and accurate methods (and codes) are in demand, of which several have been successfully applied to systems of reasonable complexity.

2. CALCULATIONS

As an example of a system of practical interest we consider the hexanuclear "ferric wheels" $MFe_6[N(CH_2CH_2O)_3]_6Cl$ (M = Li, Na, see Fig. 1), synthesized at the Institut für Organische Chemie in Erlangen [3] and labeled as substances 4 and 3 in the latter publication. These materials belong to a larger family of Fe-coronates, of which 8- and 10-member rings are also known. A common feature of these substances is the bonding of Fe atoms *via* doubled oxygen bridges, somehow resembling the 90° coupling of magnetic atoms in transition-metal oxides. In the vicinity of each Fe atom one finds a nitrogen atom, connected *via* C_2H_4 chains to oxygen atoms. The Li- and Na-centered molecules have a very similar structure, with only slightly different Fe–O–Fe angles (101.1° for Li-wheel and 103.3° for Na-wheel).
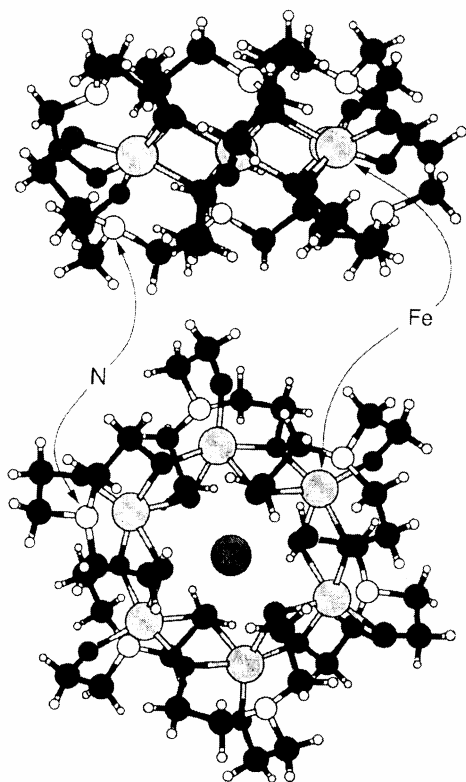
Fig. 1. The Li-centered "ferric wheel" molecule. The Li ions in the middle of the ring; the distant Cl ion included in the simulation is not shown; the rest of (electrically neutral) solvent is neglected

The interest in the magnetic properties of the system is the presence of large magnetic moments, traditionally argued to correspond to $S = 5/2$ on the Fe site, thus implying a highly ionized Fe(III) state. Such an identification of the iron magnetic moment is consistent with magnetization and torque measurements [4], from which Waldmann *et al.* derived the values of exchange parameters J for the spin Hamiltonian of the Heisenberg model:

$$H = -J \left(\sum_{i=1}^{5} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_6 \cdot \mathbf{S}_1 \right) + (\text{anisotropy term}) + (\text{Zeeman term}) \qquad (1)$$

The obtained values of J are -18 to -20 K for the Li-wheel (depending on sample and method) and -22.5 to -25 K for the Na-wheel, thus implying an antiferromagnetic (AFM) ground state. While the data from bulk magnetic measurements seem to be well established by now and reliable, virtually no spatially resolved probing of the magnetic structure has been carried out yet. Recent X-ray photoelectron and X-ray emission spectroscopy studies [5] allow to probe the electronic structure in the valence band and on the Fe site, albeit without resolution in spin. This is exactly where *ab initio* calculations may yield a valuable contribution in providing site- and spin-resolved densities of states, as well as the spatial distribution of charge and magnetization densities. The verification of these predictions demands the comparison with (atom- and/or spin-averaged) spectroscopic data, and eventually comparison with other calculational approaches at a different level of approximations.

In the present study, we compare the results of electronic structure calculations by two different methods – SIESTA [6] and NRLMOL [7]. Both methods are based on the DFT; from the various exchange-correlation functionals implemented we used the generalized gradient approximation after Perdew-Burke-Ernzerhof [8] for the present study. A further similarity is that their basis sets are atom-centered functions – numerical pseudoatomic orbitals in SIESTA [9] and contracted Gaussian-type orbitals in NRLMOL [10]. The main difference is that SIESTA uses norm-conserving pseudopotentials whereas NRLMOL is an all-electron code. NRLMOL uses the symmetry, which is relatively high in case of the Fe_6-wheels, of a molecule in question in all numerical tasks. Moreover, all computationally intensive parts of the code are massively parallelized [11], which makes DFT calculations on molecular magnets (with a typical size of 100-200 atoms) feasible. SIESTA is competitive due to the compactness and efficiency of its numerical basis sets. Moreover, it can work as an order-N method (albeit not yet for magnetic systems), solving the DFT problem without explicit diagonalization. Other features of the two calculational methods, which are potentially important in application to molecular magnets but have not been actually used in the present study, are the availability of accurate forces in both codes, the spin-orbit coupling treated within second order perturbation theory in NRLMOL [12], the possibility of general-form (i.e., non-collinear) magnetization in SIESTA [13]. Being an *ab initio* pseudopotential code, SIESTA is usually able to provide very good accuracy for the electronic structure and total energies without fitting to any exterior information, but still benchmark calculations make sense for critical cases and/or new systems. The present study serves in part exactly this task, as the accuracy of all-electron NRLMOL method is expected to be superior to that of SIESTA. As the latter is routinely used for dynamical simulations in large systems with virtually all symmetry lost, no special treatment is provided for the use of possible point group symmetries available in the molecule. For the systems in question, due to high degeneracy of energy levels close to the chemical potential, the neglect of symmetry leads to a certain instability in the convergence, which however can be managed by keeping the mixing parameter very low (10^{-3}-10^{-4}) and imposing the fixed spin moment scheme (FSM, Ref. [14]).

3. RESULTS

In the following, we discuss the results obtained by SIESTA for the Li-centered molecule, and by NRLMOL – for the Na-centered one, with the coordinates as reported from the crystallographic study of corresponding materials [3]. The NRLMOL treatment was restricted to the ground-state AFM configuration (alternating orientations of Fe magnetic moments over the ring); the SIESTA calculation addressed in addition different magnetic configurations, that allowed to make an estimate of exchange parameters.

Figure 2 displays the partial densities of states (DOS) on Fe and its several neighbors in the AFM configuration, as calculated by both methods. The discrete levels of the energy spectra are weighted (with the charge density integrated over atom-centered spheres in NRLMOL, or according to Mulliken population analysis in SIESTA), and broadened for better visibility, with broadening parameter of 0.15 eV in SIESTA and 0.14 eV in NRLMOL. The local moments corresponding to integrating such partial DOS over occupied states are given in Table I.

Table I. Local magnetic moments M at Fe and its neighbors. NRLMOL results correspond to spin density integrated over sphere of radius R centered at corresponding atom; SIESTA values are due to Mulliken population analysis

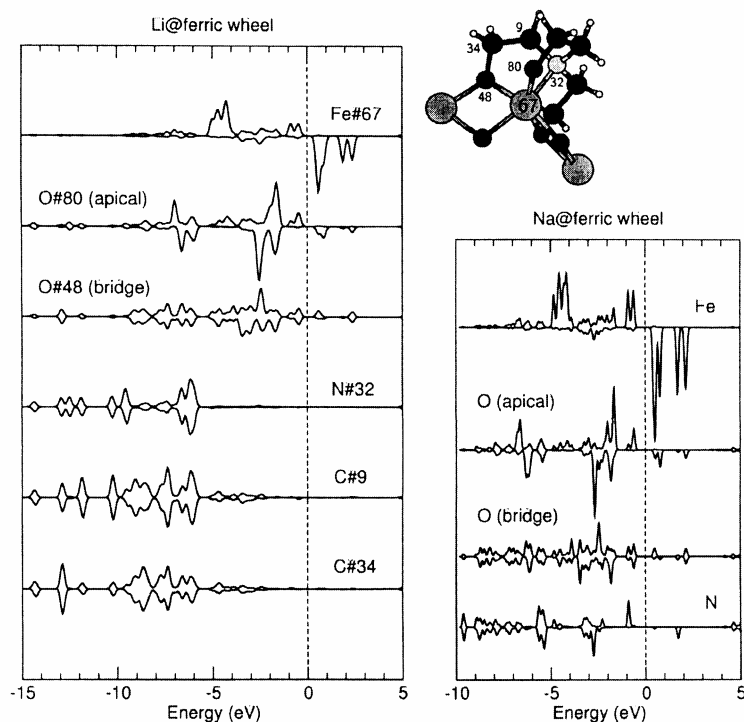| Atom	R (a.u.)	M (μ_B), NRLMOL	M (μ_B), SIESTA
Fe	2.19	3.85	3.91
O (apical)	1.25	0.20	0.30
O (bridge)	1.25	±0.01	±0.02
N	1.32	0.07	0.09

Fig. 2. Atom- and spin-resolved partial densities of states as calculated for Li-centered molecule by SIESTA (left panel) and for Na-centered molecule by NRLMOL (right panel). The DOS at the Fe site is scaled down by a factor of 2 relative to other constituents. The numbering of atoms which are neighbors to the Fe atom is shown in the inset. See text for details of calculation

One notes a remarkable agreement between both calculations up to the finest details in the distribution of state densities at Fe and O sites. This is the more astonishing as the local DOS is a loosely defined property, normally dependent on the choice of region it attributes to, or, in the present context, to the choice of basis functions which are quite differently constructed in both calculational approaches. It also indicates that there is no significant influence of the central atom (Li or Na) on the electronic structure. Using NRLMOL we calculated the total charge within a sphere with a radius of 2.97 Bohr units around the Na atom. There are already 10.98 electrons

contained inside the sphere and zero spin polarization which clearly indicates that the Na atom does not play a role for the electronic structure of the ferric wheel.

Notably, both methods find the local magnetic moments on Fe sites are very close to 4 μ_B and not to 5 μ_B as is generally assumed, based on the above mentioned magnetization data. The maximal magnetization $S = 5/2$ of the Fe atom corresponds to a Fe(III)-ion in the $3d_{\uparrow}^{5}d_{\downarrow}^{0}$ configuration. Our first-principles calculations suggest a somewhat different picture: the minority-spin DOS has a non-zero occupation due to the hybridization (chemical bonding) of Fe$3d$ with O$2p$ states. However, the magnetic polarization in the organic ligand which provides the octahedral coordination for the iron atoms due to Fe is substantial, the most pronounced effect being on the apical oxygen atom (which is not participating in the bonding to the next Fe neighbor). Taken together with the (smaller) polarization of the bridging oxygen atoms and magnetization at the nitrogen site, the distributed magnetic moment *per* Fe atom yields 5 μ_B, recovering the agreement with the magnetization results.

An important consequence is that the charge state of iron is not Fe(III) but more close to Fe(II), according to our calculations. Moreover, the distributed magnetic moment behaves like a rigid one, in a sense that it can be inverted, following a spin flip on a Fe site. This conclusion has been derived from our analysis of other magnetic configurations, done with SIESTA [5]. The local DOS does not change considerably when switching from AFM to FM configuration – only the HOMO/LUMO gap becomes less pronounced, and a slight ferromagnetic shift between the two spin bands appears. Further, the change of total energies in the sequence of FSM, from the maximal spin moment of 30 μ_B to one Fe spin inverted (20 μ_B), and then to two (second-neighbors) Fe spins inverted is linear, supporting the conclusion that the system maps well onto the Heisenberg model. The corresponding exchange parameter, as estimated over both $30\rightarrow20$ and $20\rightarrow10$ μ_B flips, is around -80 K. This yields a correct sign and correct order of magnitude, relatively to experimental estimates of Ref. [4]. However, the magnitude is overestimated by a factor of ~4. The exchange parameters J depend on the spatial overlap of the d-orbitals on different Fe-sites. It is well known that the d-orbitals within DFT are not localized enough compared to experiment, consequently the J values will be overestimated. There are two main reasons for this shortcoming. First, possible on-site correlations as known from atomic physics are underestimated in case of "conventional" DFT. Second, DFT is not free from spurious self interactions due to the replacement of the point-like electrons by corresponding densities. Bringing in the atomic physics in the form of LDA + U (adding a local orbital dependent atomic Coulomb interaction parameter U to DFT, [15]) or self interaction corrections (SIC) [16] will improve the results by lowering the d-orbitals in energy and therefore localizing them stronger. SIC only affects occupied states, whereas LDA + U plunges the occupied d-states and shifts the unoccupied ones to higher energies. By increasing, on the average, the magnetic excitation energy across the spin majority-minority gap, both mechanisms help to effectively reduce the magnitude of J. In what regards the LDA + U approach, this has been shown by Boukhvalov *et al.* for another molecular magnet, Mn$_{12}$ [17].

It is worth noting that the inversion of the third Fe spin that yields the AFM configuration does not follow the same linear trend. The origin of this is not clear at the moment and should be tested in further high-precision calculations. We recently became aware of calculations by E. Ruiz on similar systems [18], done also with the use of SIESTA. According to them, the J values

extracted just from the FM-AFM total energy difference along the procedure described in Ref. [19] yielded the J values of $\approx$ -24 K (Li system) and $\approx$ -45 K (Na-system). A similar estimate from FM to AFM transition with our total energy data gives -38 K, i.e., such estimates seem to be in better agreement with the reported experimental data. It remains to be tested, however, whether the FM to AFM transition can be reasonably well fitted to the Heisenberg model with a single (nearest-neighbors) exchange parameter, in view of above mentioned nonlinear dependence of the total energy on the total spin. In V_{15}, another molecular magnet, a complex system of six exchange parameters was found to be necessary [20] in an otherwise conceptually similar fit to the Heisenberg model.
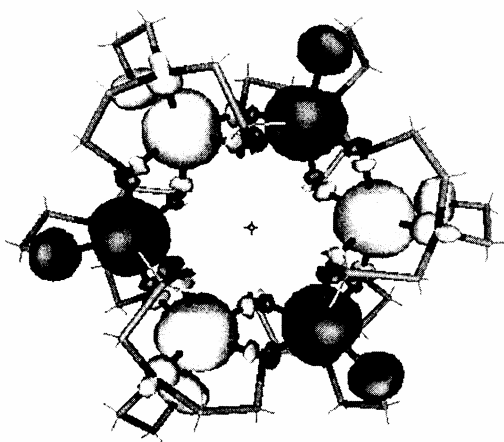

Fig. 3. Plot of the spin density map calculated with NRLMOL. The isosurfaces correspond to $\pm 0.01 e/\text{Å}^3$. While most of the magnetic moment is localized at the Fe atoms, there is still some spin polarization on O and N

A clear visualization of the above discussed delocalized (or, rather, distributed) magnetic moment associated with the Fe atom comes from the map of spin density, obtained from the NRLMOL calculation (Fig. 3). One should take into account that the volume enclosed by the iso-surfaces is not directly correlated to the total moment at the site. One sees moreover an absence of magnetization on carbon and hydrogen sites. The fact that the magnetization is noticeable and changes its sign when passing through bridge oxygen atoms emphasizes the failure of methods depending the spherical averaging of atom-centered potentials. From the side of experiment, it would be interesting to probe the spin polarization on oxygen and nitrogen atoms.

4. CONCLUSION

We presented a study of the electronic structure of a six-membered ferric wheel with Li or Na as a central atom. The local densities of states on the iron and neighboring sites clearly indicate that the magnetic moment is distributed over several sites. The local moment at the iron site is still the largest one with about $4\,\mu_B$, although indicating that the iron in the ferric wheels is closer to Fe(II) than Fe(III) as generally expected. The local spin of $S = 5/2$ per iron site as deduced from magnetization measurements is reproduced if one takes the moments on the neighbor atoms into account. The largest moment is found on the apical oxygen atom, followed by smaller moments on nitrogen and the bridging oxygen atoms. This picture has been confirmed by a plot of the spin

density map. A further goal of the present study has been a comparative test of two different DFT implementations. In most cases the local (energy-resolved) DOS and (spatially resolved) magnetization density show a very good quantitative agreement. The most pronounced deviations are related to nitrogen, indicating less localized magnetic moment there and thus higher sensitivity of numbers to the exact normalization of DOS.

In order to explore the range of systems where the presented first-principles methods give reliable results, further studies on more systems are required. In particular studies of experimentally well characterized classes of compounds where only the ligands are changed in a controlled way but not the magnetic core would reveal if our calculational approach can reproduce the observed changes in the magnetic behavior. Our current results make us very confident in the predictive power of the presented methods. This should allow for a microscopic understanding based on the electronic structure of single molecule magnets.

Acknowledgments

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