論文の内容の要旨

論文題目　*Ab initio* prediction of magnetic structures
(磁気構造の第一原理予測)

氏名　フブシ・マリーテレス (Marie-Therese Huebsch)

The grand challenge in first-principles calculation for magnetic materials is whether we can predict the experimental magnetic structure for a given material. Among a variety of possible functional materials, noncollinear magnets are a fascinating playground for materials design as they facilitate a wide range of fundamental phenomena and possible applications.

For example, in the context of antiferromagnetic (AFM) spintronics (1) there is a particular interest in noncollinear antiferromagnetism sparked by (i) its robustness against perturbations due to magnetic fields, (ii) a quasi-absence of magnetic stray fields disturbing for instance nearby electronic devices, and (iii) ultrafast dynamics of AFM domainwalls (2), as well as (iv) its ability to generate large magnetotransport effects (3). Hence, the optimization of AFM materials would open the door for applications such as seamless and low-maintenance energy generation, ulrafast spintronics and robust data retention, as well as be a guide towards advancing fundamental understand- ing of magnetotransport.

However, first-principles calculations with the generalized gradient approximation (GGA) in the framework of spin-density functional theory (SDFT) for magnetic materials have a problem: It is still an open question how accurately SDFT—GGA can reproduce the experimental magnetic ground state. While SDFT has been widely used in studies on various magnets (4), there has been no systematic benchmark calculation for noncollinear AFM materials. Previous attempts have been restricted to collinear magnetism (5) or even stricter symmetry constraints (6–8). In regard to noncollinear AFM materials, high-throughput calculations have been limited to setting the experimentally determined magnetic configuration as an initial guess (9). A recently proposed attempt to predict magnetic structures based on a genetic evolution algorithm (10) strongly relies on the proper prediction of the magnetic ground state by SDFT. The lack of a systematic benchmark calculation is a consequence of the fact that it is a highly non-trivial task to investigate all the local minima in the SDFT energy landscape. Indeed, to search for all the (meta-)stable states, we need an exhaustive list of physically reasonable magnetic configurations for which first-principles calculations can be performed.

To this end, we devise the so-called cluster multipole (CMP) theory (11), which enables the expansion of an arbitrary magnetic configuration in terms of an orthogonal basis set of magnetic multipole configurations. By means of the CMP expansion, a list of initial magnetic structures for self-consistent GGA calculations is efficiently and systematically generated. With this at hand, we performed a systematic high-throughput calculation with 2935 calculations. With our scheme termed CMP+SDFT we have predicted magnetic structures for 131 materials, which have been subsequently cross-checked with the experimental data found on the experimental database MAGNDATA (12). As can be seen by referring to Ref. (13), we thoroughly discussed the following questions:

I. Is the CMP expansion a physically meaningful description of magnetic configurations? Namely, here the premise for a physically meaningful description constitutes that naturally occurring magnetic configurations can be characterized by one or few symmetrically related CMPs. It can be understood in the same sense as atomic orbitals are a meaningful basis to describe electrons bound to a free atom, i.e. the probability distribution of one electron is

described by one or few degenerate atomic orbitals. In fact, this analogy extents to molecular orbitals in a complex, where the underlying spherical harmonics are symmetrized according to site symmetry.

II. Can GGA predict the most stable magnetic configuration by the aid of an exhaustive list of candidate magnetic configurations for a given crystal? In fact, the predictive power of the combination of the CMP expansion and SDFT (CMP+SDFT) ought to be seen as a composition of the following issues:

   A. Is there evidence to assume that the list of candidate magnetic configurations generated by the CMP basis is exhaustive?

   B. Can the experimentally determined magnetic configuration be found among all GGA results?

   C. Can GGA correctly assign the lowest total energy to the experimental magnetic configuration?

III. Is the on-site magnetic moment estimated by CMP+GGA close to the experimentally determined magnetic moment per site?

We find that materials existent in nature are well-described in terms of only few CMPs and infer the CMP expansion basis to be a suitable basis for magnetic configurations. Additionally, the experimental data suggests that the magnetic ground state favors either pure CMPs or linear combinations of CMPs having the same expansion order and same irreducible representation. Guided by this heuristic rule an exhaustive list of initial candidate magnetic configurations for GGA calculations is created.

The high-throughput calculation of 2935 LSDA calculations using VASP led to a handful of CMP+GGA local minima corresponding to different possible magnetic configurations for each material. 90.16% of materials yield the experimental magnetic space group for at least one of the CMP+GGA local minima. Furthermore, the maximum overlap between the experimental magnetic configuration and the CMP+LSDA local minima exceeds 0.75—with 1 corresponding to equivalence—in 70.99% of all materials.

An *ab initio* prediction of the most stable magnetic configuration in the experiment is guided by a comparison of the total energy in GGA of the the possible magnetic configurations for each material. In particular, the local minimum with the larges overlap with the experiment (MaxOExp) is expected to yield the lowest total energy. Indeed, for materials featuring magnetic sites with *d*-orbital magnetism, MaxOExp is in great majority of the cases less than 1meV above the so-called CMP+SDFT global minimum. On the other hand, the same could not be confirmed for *f*-orbital magnetism. In fact, MaxOExp for *f*-orbital magnetism shows no tendency towards lower total energy. The implementation of GGA used in this study did not necessarily assign the lowest total energy to the local minimum with the larges overlap with the experiment. Nevertheless, we want to emphasize that CMP+GGA succeeded to narrow down the number of possible magnetic ground states. This is achieved in parts thanks to a list of candidate magnetic configurations that is tailored to account for details of the symmetry of the crystallographic unit cell. With this CMP enables SDFT to identify a feasible number of local minima, that put data screening and AFM material design within reach.

In addition, this study showed that the on-site magnetic moment could be estimated surprisingly well by GGA. The precision of the predicted magnetic moment is estimated to be roughly $\pm 0.5 \mu_B$. Some outliers arise from a lack of long-range order in the experiment. This can be due to extremely low transition temperatures but also due to magnetic frustration. Despite some explainable outliers, the prediction shows no major systematic over- or underestimation of the on-site magnetic moment in GGA. In contrast to the experiment, the GGA calculation grants additional insight into the balance of spin contribution and orbital angular momentum contribution to the total magnetic moment, as shown in

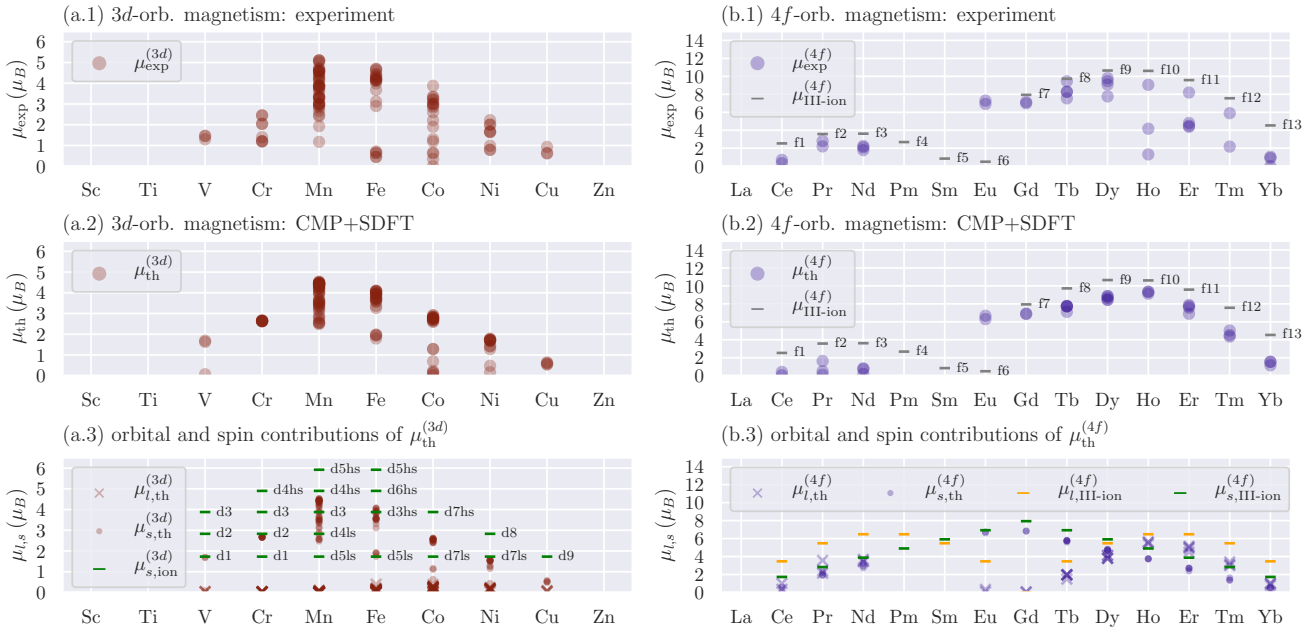

Figure 1. 3*d*-orbital magnetism proves to be well-described by Russel-Saunders coupling applicable within the strong field regime. The orbital angular momentum is quenched and the spin-only ionic limit can be used as a reference. The case of lanthanides, on the other hand, is representative for systems in the weak field regime. The on-site magnetic moment is well-described in the j-j coupling scheme. We speculate that GGA might have slightly overestimates the crystal field effects compared to the strength of spin-orbit coupling. This could explain why materials governed by crystal field splitting—such as the compounds with d-orbital magnetism—are assigned appropriate total energy by GGA. Yet, materials governed by spin-orbit coupling—such as lanthanides—the experimental magnetic configuration is not assigned the lowest total energy by GGA. We strongly believe that this benchmark provides a solid foundation for the *ab initio* predictions of various magnetic properties.

The thesis is structured as follows: In Chapter 1, we take a birds eye view on magnetism and in particular motivate the search for novel magnetic structures realized in crystalline compounds, that feature transition metals, lanthanides and actinoides as magnetic sites. In Chapter 2, we introduce the framework of SDFT for noncollinear magnetic structures. In Chapter 3, the multipole theory is first developed generally to expand a vector gauge field characterized by the vector Poisson equation. Subsequently, this theory is applied to magnetic structures in real materials to arrive at a scheme to generate a symmetry-adapted orthogonal basis set of magnetic configurations in the crystallographic point group. This is the so-called CMP theory.

In Chapter 4 we present the central results of this thesis. Here, we discuss a benchmark calculation of 131 materials, those magnetic ground state is predicted in a high-throughput CMP+SDFT scheme. Moreover, we investigate the effects of Coulomb repulsion U on the prediction of the most stable magnetic configuration, as well as the size of the magnetic moment. Based on these practical insights, we revisit SDFT in Chapter 5. This shall set the stage for a new question: Namely, how can we improve existing exchange--correlation functionals in order to accurately reproduce the experimental magnetic ground state in the framework of SDFT. A summary and outlook is presented in Chapter 6.

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