Study of magnetic nanoparticles at the atomic scale based on spin models from first principles

PhD Thesis Booklet

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Background

Thanks to the rapid development of the fabrication techniques in nanotechnology, the building blocks of several nanodevices reached the atomic scale. Scientists and engineers have to face, however, the fact that the fluctuations can destroy the functionality of these building blocks, posing a big challenge to maintain the rate of technological development. As an example, the superparamagnetic behavior of small ferromagnetic particles sets the size limit for data storage, because the activation energy (energy barrier), E_a, between two stable states of the particle is proportional to the volume of the particle. The Néel relaxation (average switching) time of such particles scales as $\exp(-E_a/k_BT)$, where k_B is the Boltzmann constant and T is the temperature, leading to very low blocking temperatures as the size of the nanoparticles is reduced. This problem can be solved by utilizing the large perpendicular magnetic anisotropy (PMA) provided in thin films.

Due to possible applications in quantum computing, magnetic–superconducting heterostructures came into the focus of experimental and theoretical research during the past decade. In the presence of magnetic impurities in a superconductor, the coupling between the magnetic moment and the Cooper pairs gives rise to the so-called Yu–Shiba–Rusinov (YSR) states, which could be measured in several systems (see e.g. [III]). In atomic chains, these YSR states evolve into bands, that can lead to the appearance of Majorana edge states [1]. Because of their topological properties, the Majorana fermions are less sensitive to fluctuations, therefore, they are promising candidate for realizing quantum bits. In a recent paper by Beck *et. al.* [III], a Mn adatom and Mn dimers were investigated on superconducting Nb(110) and the experimental results were supported by tight-binding model calculations with parameters based on density functional theory calculations. It was shown that the YSR states hybridize not only in ferromagnetic, but also in antiferromagnetic dimers, as a consequence of the spin-orbit coupling (SOC). Determining the magnetic configuration is, therefore, of crucial importance to explain the splitting of the YSR states.

From a theoretical point of view, embedded cluster techniques combined with the Korringa–Kohn–Rostoker Green's function (KKR-GF) formalism proved to be extremely useful to study supported small nanoparticles [2]. This technique made possible to investigate a large variety of magnetic nanoparticles, with special emphasis on the magnetic anisotropy of adatoms and small clusters [V], on canted ground state of monatomic chains, on the magnetism of quantum corrals, on magnetic interactions, and on chiral magnetic patterns in nanoclusters [I].

Classical spin models are frequently used to determine the ground state magnetic configuration and study the finite-temperature magnetism of magnetic nanostructures. To increase the accuracy of such simulations, the parameters of the spin Hamiltonians can be calculated from first principles. Exchange interactions between magnetic atoms in terms

of the relativistic torque method (RTM) [3] were used for atomistic spin-model simulations making possible to generate an extended spin Hamiltonian including the Dzyaloshinskii–Moriya interaction (DMI), as well as an atomic resolution of the magnetic anisotropy, that can induce noncollinear ground state spin configurations.

Another widely used method to calculate magnetic interactions from first principles is the spin-cluster expansion (SCE) technique as combined with the relativistic disordered local moment (RDLM) scheme [4]. A great advantage of the method is that it provides a systematic (irreducible) set of multispin interactions, and the spin-model parameters can uniquely be obtained without the assumption of any arbitrarily ordered reference states. Moreover, the correct symmetry of the exchange interaction and anisotropy matrices is *a priori* granted as dictated by the symmetry of the corresponding lattice site.

Considering only two-spin interactions in the spin model is not sufficient to describe all types of magnetic order. It was demonstrated in various ultrathin film systems that isotropic four-spin interactions may stabilize up-up-down-down states, conical spin spirals, or nanoskyrmion lattices. The strategy of including higher-order terms in the spin Hamiltonian was applied with success for magnetic clusters. Brinker et al. [5] provided a systematic way to track down all the spin interactions up to fourth order relying on the spin-cluster expansion within the framework of the full potential Korringa–Kohn–Rostoker Green's function method including the spin-orbit coupling. However, a few recent works have advanced unwarranted interpretations of their first-principles calculations, such as chiral three-spin interactions that are incompatible with time-reversal symmetry, or a very large DMI [6, 7] that depends strongly on the magnetic configuration and does not rely on the spin-orbit coupling.

Objectives and summary of the research

Motivated by the previously mentioned experimental studies on nanomagnet-superconductor systems and by recent results on higher-order spin-spin interactions, my PhD research was related to the investigation of small magnetic nanoclusters deposited on metallic surfaces. The main purpose my research was to explore the origin of the magnetic ground state of these systems based on suitable spin models. An additional aim of my research was to compare different methods used to derive spin model parameters and to study the effect of higher-order spin interactions.

My theoretical investigations mostly rely on deriving tensorial spin-spin interactions in terms of the RTM and the SCE. In addition, I developed a Green's function perturbation method (PM) suitable to calculate higher-order interactions. Related to the PM, I give a comprehensive review of isotropic, multispin model parameters and I introduce a multisite multispin Hamiltonian that can conveniently be used in applications. Moreover, I discuss how the four-spin interactions enter the local two-site interaction calculated within the

torque method and give explicit expressions for the configuration dependent spin-model parameters derived for non-collinear spin structures in [6, 7].

The thesis contains the theoretical study of three types of magnetic nanostructures. First, I investigated the magnetic properties of monatomic Fe chains on the Re(0001) substrate, for which experimental results are available in [1]. I found that the 15-atom-long chain has a spin-spiral ground state with both in-plane and out-of-plane components of the magnetization, in agreement with the experiments. I conclude that including chiral four-spin interactions is necessary to resolve contradictory results between the spin model and the direct *ab initio* calculations. Next, I investigated Mn and Fe clusters (adatoms, dimers, and chains) deposited on Nb(110). I performed analytical calculations for the ground state spin configuration for the dimers. For the dimers and the chains, I validated the calculated isotropic Heisenberg interactions in terms of band energy differences between ferromagnetic and antiferromagnetic configurations. My final study is related to equilateral trimers of Mn and Cr atoms on Au(111) surface, for which I applied the perturbation method to determine two-spin and four-spin interactions. I compared the accuracy of the spin models based on the torque method, on the spin-cluster expansion and on the perturbation method in terms of a statistical method. In addition, along a continuous path in the configuration space, I numerically evaluated the two-spin variations of the energy and the configuration dependent two-spin interactions. I demonstrated that the strong configuration dependence of these parameters arises exclusively from the isotropic four-spin interactions.

New scientific results

The new results in my thesis are summarized in the following thesis statements:

1. I investigated the magnetic properties of finite close-packed Fe chains on Re(0001) surface using a classical spin model, where the parameters were determined by the relativistic torque method. From the minimization of the energy an antiferromagnetic ground state was found for the 5-atom-long chain, while in the case of the 10- and 15-atom-long chains the formation of spin spirals was inferred. Based on the Fourier transform of the isotropic interactions, I demonstrated that the spin-spiral formation was the consequence of the frustration of the isotropic couplings in the chains. The chirality of the spin spirals were determined by the Dzyaloshinskii–Moriya (DM) interactions between the Fe atoms. Moreover, the spin spirals appeared to be tilted with respect to the plane of the surface due to the interplay of the DM interactions and the magnetic anisotropy as I showed by using a simplified spin model. These results are published in paper [I].

2. In order to test the validity of the spin-model results, I calculated the *ab initio* band energy of homogeneous spin spirals for the 15-atom-long Fe chain on Re(0001) as a function of the wavenumber and the tilting angle. While the wavenumber of the lowest-energy homogeneous spin spiral was in good agreement with that obtained from the spin-model simulations, it turned out that the two spin-spiral states had opposite chirality related to the normal-to-plane component of the DM vectors. In order to resolve this contradiction, I developed a rotational scheme to evaluate the DM vectors by mapping a considerably larger region in the spin-configuration space than in the case of the torque method. Indeed, it turned out that the z-component of these DM vectors had the sign in accordance with the chirality of the spin spiral obtained from the band energy calculations. I explained the different results for the DM vectors by the effect of emergent fourth-order chiral interactions. These results are published in paper [I].

3. I calculated the electronic and magnetic properties of Mn and Fe adatoms and clusters of adatoms on Nb(110) surface. In terms of a classical spin model with parameters calculated from the spin-cluster expansion, I determined the ground state of Mn and Fe dimers, as well as monatomic chains along different crystallographic directions. The dimers turned out to have almost collinear, either ferromagnetic or antiferromagnetic, configurations with very small canting angle. I developed analytical approximations for calculating these canting angles and obtained good agreement with the numerical simulations. In agreement with available experiments, I showed that the strong nearest neighbor isotropic interactions lead to almost collinear spin configurations in the ground state of the chains, except the Fe chains along the $[1\bar{1}0]$ direction, which has a spin-spiral ground state due to the frustration of the isotropic couplings. These results are published in papers [II] and [III].

4. For the nearest neighbor Mn and Fe dimers on Nb(110) along three different crystallographic directions, I analyzed the calculated isotropic couplings in terms of local density of states as projected onto symmetry adapted orbitals and corresponding band energy differences. I demonstrated that the band energy difference between the ferromagnetic and antiferromagnetic configurations fits almost perfectly the isotropic coupling calculated by the spin-cluster expansion. Moreover, the band energy sorted out according to canonical orbitals and the orbital decomposition of the isotropic coupling are also related qualitatively well to each other. I showed that the nearest neighbor isotropic couplings are more sensitive to the coordination number for the Fe chains than for the Mn chains, which was understood by the difference of the band energies between the FM and the alternating AFM configurations. These results are published in paper [II].

5. I developed a non-relativistic perturbation technique to determine isotropic two-spin and four-spin interactions within the framework of the Korringa–Kohn–Rostoker Green's function formalism and implemented it into the Embedded Cluster KKR code. I applied the new method to equilateral Mn and Cr trimers deposited on the Au(111) surface and compared the parameters with those obtained by using the torque method and the spin-cluster expansion. I showed explicitly that the two-site exchange couplings derived from the torque method are a combination of two-spin and four-spin (in general, any higher-order) interactions. Using a statistical approach based on random configurations I demonstrated that the spin-cluster expansion and the perturbation method adequately map the band energy, but the torque method remarkably underestimates the isotropic interaction for both trimers. These results have not been published yet.

6. Based on the spin Hamiltonian containing two-spin and four-spin isotropic interactions, I determined the two-spin rotation energies and derived explicit expressions for three types of configuration dependent two-site interactions termed as the isotropic, Dzyaloshinskii–Moriya and anisotropy interactions in Refs. [6, 7]. I showed that the configuration dependent Dzyaloshinskii–Moriya and anisotropy interactions appear only for non-collinear spin configurations and are the consequence of the four-spin (higher-order) interactions. I calculated these quantities for equilateral Mn and Cr trimers along a continuous path from a ferromagnetic to a co-planar Néel state, and demonstrated that the parameters strongly depend on the configuration. I argued that the configuration dependent parameters can only be used to quantify the second derivative of the energy, but they are not suited to define a spin-model, i.e. to directly determine the energy of the system. The criticism of the configuration dependent Dzyaloshinskii–Moriya interaction is published in paper [IV]. The numerical results have not been published yet.

Publications related to the thesis statements:

[I] A. Lászlóffy, L. Rózsa, K. Palotás, L. Udvardi and L. Szunyogh, *Phys. Rev. B* **99**, 184430 (2019)

[II] A. Lászlóffy, K. Palotás, L. Rózsa and L. Szunyogh, *Nanomat.* **11**(8), 1933 (2021)

[III] P. Beck, L. Schneider, L. Rózsa, K. Palotás, A. Lászlóffy, L. Szunyogh, J. Wiebe and R. Wiesendanger *Nat. Commun.* **12**, 2040 (2021)

[IV] M. dos Santos Dias, S. Brinker, A. Lászlóffy, B. Nyári, S. Blügel, L. Szunyogh, and S. Lounis, *Phys. Rev. B* **103**, L140408 (2021)

Other publication related to the PhD Thesis:

[V] A. Lászlóffy, L. Udvardi and L. Szunyogh, *Phys. Rev. B* **95**, 184406 (2017)

References

[1] Kim, H., Palacio-Morales, A., Posske, T., Rózsa, L., Palotás, K., Szunyogh, L., Thorwart, M., and Wiesendanger, R. *Sci. Adv.* **4**(5), eaar5251 (2018).

[2] Lazarovits, B., Szunyogh, L., and Weinberger, P. *Phys. Rev. B* **65**(10), 104441 (2002).

[3] Udvardi, L., Szunyogh, L., Palotás, K., and Weinberger, P. *Phys. Rev. B* **68**(10), 104436 (2003).

[4] Deák, A., Szunyogh, L., and Újfalussy, B. *Phys. Rev. B* **84**(22), 224413 (2011).

[5] Brinker, S., dos Santos Dias, M., and Lounis, S. *Phys. Rev. Research* **2**, 033240 (2020).

[6] Cardias, R., Bergman, A., Szilva, A., Kvashnin, Y. O., Fransson, J., Klautau, A. B., Eriksson, O., and Nordström, L. *arXiv:2003.04680* (2020).

[7] Cardias, R., Szilva, A., Bezerra-Neto, M. M., Ribeiro, M. S., Bergman, A., Kvashnin, Y. O., Fransson, J., Klautau, A. B., Eriksson, O., and Nordström, L. *Sci. Rep.* **10**, 20339 (2020).