Monte Carlo study on magnetic nanoparticles from first principle

László Balogh[1], Kristof M Lebecki[2], Bence Lazarovits[3], László Udvardi[1], László Szunyogh[1] and Ulrich Nowak[2]

[1] Department of Theoretical Physics, Budapest University of Technology and Economics, H-1111 Budafoki út 8., Budapest, Hungary
[2] Fachbereich Physik, Universität Konstanz, D-78464 Konstanz, Germany
[3] Research Institute for Solid State Physics and Optics, HAS, Konkoly-Thege Miklós út 29-33, Budapest, Hungary

E-mail: udvardi@phy.bme.hu

Abstract. In order to study the finite temperature behavior of magnetic nanoparticles a novel Monte Carlo method has been developed. The energy of a new trial configuration during the simulation is calculated directly from the expansion of the band energy avoiding a set up of an *a priori* Heisenberg-type model. The electronic structure of the cluster is determined by means of the embedded-cluster Green's function technique based on the Korringa–Kohn–Rostoker method within the local spin-density approximation of the density functional theory. As a benchmark the ground state of anti-ferromagnetic clusters and the temperature dependence of the magnetization of a flat square cluster of 16 Co atoms on a Cu(001) surface have been studied.

1. Introduction

Nano-sized magnetic structures get particular attention nowadays, because of their promising perspective in magnetic data storage technology. A large amount of experimental [1, 2] and theoretical [3, 4] work is currently focusing on magnetic systems with reduced symmetry such as thin films and atomic size clusters.

The magnetic properties of a wide class of systems are often described by the classical Heisenberg model,

$$\mathcal{H} = \frac{1}{2} \sum_{i,j} J_{ij} \boldsymbol{\sigma}_i \boldsymbol{\sigma}_j, \tag{1}$$

where $\boldsymbol{\sigma}_i$ is a unit vector pointing along the magnetization at site i and J_{ij} is the exchange coupling between site i and site j. In order to include the effect of the spin-orbit coupling, which turned out to be important for low dimensional systems [5], the model in Eq. (1) can be extended by using tensorial exchange couplings and by additional on-site anisotropy terms. For layered systems the coupling constants exhibit translational symmetry and the symmetry of the lattice structure determines the form of the on-site anisotropy. For (001) and (111) surfaces of cubic materials, e.g., the leading on-site term is an uniaxial anisotropy. However, in the case of magnetic clusters the translational symmetry is removed and the parameterization of the on-site anisotropy gets complicated due to the reduced symmetry of the system. Moreover, theoretical

studies on small Cr clusters on Au (111) surface pointed out [6] that higher order spin-spin interactions must not be neglected in the model. In order to overcome these complications, in this work we present a new scheme for Monte Carlo (MC) simulations where the change of the energy for every MC step is calculated directly from the electronic structure of the cluster.

In the next sections the method is briefly described and applications for the ground state of frustrated antiferromagnets and a comparison with a MC study based on a Heisenberg model are presented.

2. Computational method

The electronic structure of the cluster deposited on surface has been calculated by means of the embedded-cluster Green's function technique based on the fully relativistic screened Korringa–Kohn–Rostoker method [7] within the local spin-density approximation of the density functional theory. The energy of the different magnetic configurations is determined by using the band energy within the magnetic force theorem [8]. In our approach the electronic and magnetic degrees of freedom are adiabatically decoupled [9], which allows for a calculation of the energy $E\{\boldsymbol{\sigma}\}$ of any spin-configuration $\{\boldsymbol{\sigma}\}$.

In the Monte Carlo simulations the Metropolis algorithm has been applied with single spin flip dynamics to ensure detailed balance. The trial step of the algorithm is a small rotation of a randomly chosen spin arround its current direction, a choice which is symmetric and guarantees ergodicity [10]. The calculation of the band energy of each trial configuration would be extremely time consuming. In order to make the procedure numerically feasible the band energy is expanded up to second order around a given configuration $\{\boldsymbol{\sigma}_0\}$,

$$E \approx E_0 + \sum_{i=1}^{N} \frac{\partial E_b}{\partial \boldsymbol{\sigma}_i}\bigg|_{\{\boldsymbol{\sigma}_0\}} \Delta\boldsymbol{\sigma}_i + \frac{1}{2} \sum_{i,j=1}^{N} \Delta\boldsymbol{\sigma}_i^{\mathrm{T}} \frac{\partial^2 E_b}{\partial \boldsymbol{\sigma}_i \partial \boldsymbol{\sigma}_j}\bigg|_{\{\boldsymbol{\sigma}_0\}} \Delta\boldsymbol{\sigma}_j, \tag{2}$$

where the derivatives of the band energy with respect of the transverse change of the magnetization can be analytically calculated by using the Lloyd's formula [11]. To maintain the accuracy of the expansion, the trial direction of the magnetization is restricted to the vicinity of the expansion center $\{\boldsymbol{\sigma}_0\}$. After several MC steps the derivatives are recalculated for the new configuration and the trial directions are chosen around the new expansion center in order to ensure the ergodicity of the procedure.

3. Results

As a simple test the ground state of an equilateral chromium trimer on a gold (111) surface was studied by means of simulated annealing. Due to the antiferromagnetic couplings between the Cr atoms this is the simplest example of a frustrated system. The ground state turned out to be a 120° Néel-structure as shown in Figure 1 (a) and in agreement with other theoretical works [12, 6]. It is worth mentioning that the degeneracy of the two kinds of Néel structures with different chirality indices is lifted by the Dzyaloshinsky–Moriya (DM) interaction as it is detailed in Ref. [6]. For a cluster of 36 chromium atoms ordered in an equilateral triangular system on a Au (111) surface the simulations resulted in a non-collinear magnetic ground state (see Figure 1 (b)) resembling the 120° Néel-structure. A similar ground state is reported for a Cr monolayer on Cu(111) [13].

For a further test of our new type of finite temperature simulations, the temperature dependence of the magnetization of a square-shaped cobalt clusters deposited on a Cu (100) surface was compared with the results of a MC simulation based on a classical Heisenberg model. The exchange couplings were determined for an 4×4 cluster using the method described in Ref. [11]. An enhancement of the nearest neighbor exchange couplings has been found at the corners and the edges of the cluster, while inside the cluster they have very similar values to the
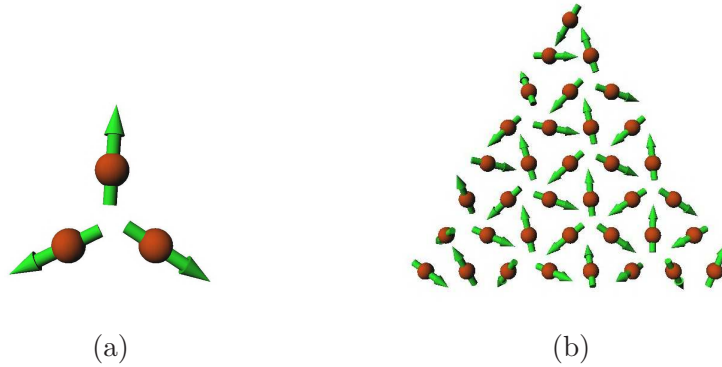
(a)   (b)

Figure 1. Ground state of the equilateral Cr_3 (a) and Cr_{36} (b) clusters on a Au(111) surface obtained from MC simulations. The arrows show the direction of the spin-magnetization.

nearest neighbor exchange in a complete monolayer. Interestingly, an opposite tendency has been seen for the magnetic moments. The nearest neighbor couplings for the non-equivalent pairs and the magnetic moments are summarized in Table 1. In the Heisenberg model only the isotropic part of the exchange coupling and an easy-plane, uniaxial anisotropy were taken into account. The anisotropy constant was chosen to be the same as that of a monolayer ($K = 0.0228\,\text{mRyd}$).

For comparison, the thermal average of the square of the magnetization of the cluster was calculated by the two methods. At a given temperature 10^5 and 10^4 MC steps were performed in the Heisenberg and in the ab-initio MC simulations, respectively. Since the magnetic anisotropy is small for the present system, the simulation based on the Heisenberg model was expected to give similar dependence of the magnetization on the temperature as our ab-initio simulation. The two result are in good agreement as shown in Figure 3.
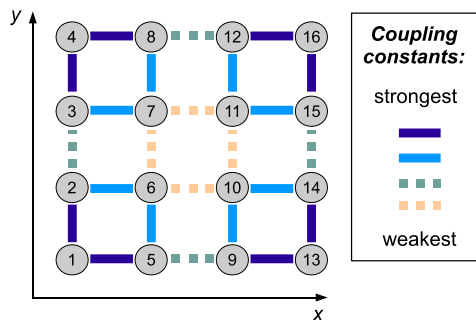

Figure 2. Nearest neighbor couplings between the atoms in the 4×4 size cluster.

Table 1. Nearest neighbor coupling constants and magnetic moments for the 4×4 Co cluster and the mono-layer.

Coupling constants	[mRyd]	Magnetic moments	$[\mu_B]$
J_{1-5}	5.59	m_1	1.74
J_{5-6}	5.27	m_5	1.82
J_{5-9}	4.49	m_6	1.87
J_{6-10}	4.19		
$J_{\text{mono-layer}}$	4.26	$m_{\text{mono-layer}}$	1.88

In order to check how accurately Eq. 1 describes the energy of the different magnetic configurations a simple test has been performed. The magnetic orientation at site i was rotated around the (100) axes while the other spins were kept frozen in the (001) direction. In the case of the Heisenberg model the energy of the system is then given as $E = \cos(\vartheta) \sum_j J_{ij}$. This energy was compared to the energy provided by the embedded cluster calculation which was done on the same magnetic configuration. Interestingly, the amplitude of the curve obtained from the electronic structure calculations was 15% larger than the one from the Heisenberg model. Including the simplest fourth order term the deviation decreased to 7%.
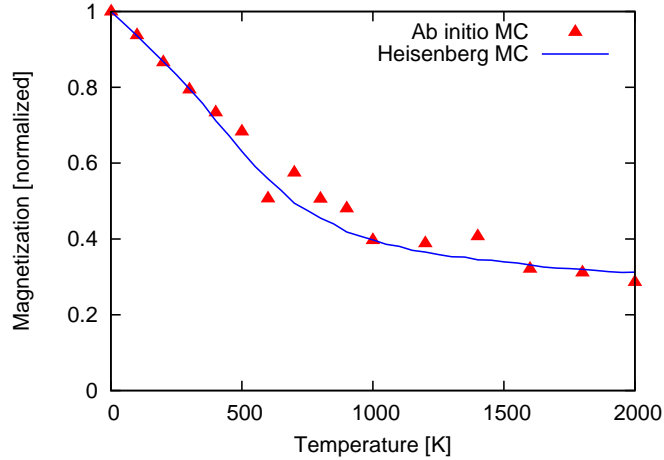
Figure 3. Square root of the thermal average of the square of the magnetization for a 4×4 Co cluster on a Cu(001) surface. The solid line represents the magnetization of the Heisenberg model, points refer to the *ab-initio* MC result.

4. Conclusions

We developed a new Monte Carlo method which avoids a setup of an *a priori* model Hamiltonian. The energy changes during the simulation are determined directly from electronic structure calculations. Relativistic effects such as magnetic anisotropy and DM interactions are naturally included through the fully relativistic treatment of the electronic structure. As a benchmark we determined the magnetic ground state of a frustrated antiferromagnetic systems and we reproduced the magnetic behavior of a small Co cluster at finite temperature. We expect that the novel method becomes a useful tool to explore magnetic properties of nano systems.

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