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Spin-cluster expansion: Parametrization of the general adiabatic magnetic energy surface with *ab initio* accuracy

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Based on the adiabatic approximation, a method for the evaluation of magnetic interactions in solids is presented which includes arbitrarily complex multispin interactions on the atomic level with *ab initio* accuracy. The spin-cluster expansion method thereby allows the accurate and fast treatment of the energetics of spin-canted systems and of the dynamic and thermodynamic properties in adiabatic approximation. It comprises the cluster expansion method of a generalized Ising model that is frequently employed in alloy theory.

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I. INTRODUCTION

The investigation of strongly noncollinear spin systems is indispensable for engineering magnetism on the nanoscale. Examples for noncollinear spin systems are domain walls on the atomic scale in quasi-one-dimensional Fe nanostripes[1] on W(110), magnetization singularities in the interior of spin curl structures,[2] and noncollinearities in small magnetic clusters or magnetization reversal processes in small systems.[3]

For a theoretical modeling of such situations the coarse graining inherent in the continuum approach of micromagnetism is not appropriate and has to be replaced by atomistic calculations. The use of the *ab initio* density functional electron theory for noncollinear spin systems[4–11] thereby yields highly accurate results but is extremely costly for nanoscale materials. An often used alternative approach[12] therefore models the dominant spin interactions, i.e., the exchange interactions, within the framework of the classical nearest-neighbor Heisenberg model,

$$E_H = -\sum_{i<j} J_H(\boldsymbol{M}_i \cdot \boldsymbol{M}_j), \tag{1}$$

where J_H is the nearest-neighbor exchange coupling taken as independent of the positions of the interacting atoms in the nanostructure. In most simulations of static and dynamical phenomena in nanostructures the quantum character of the spin is totally neglected,[12] i.e., the $\boldsymbol{M}_i$ represent classical spin variables. Thereby it is assumed that the magnitudes $|\boldsymbol{M}_i|$ of the atomic moments $\boldsymbol{M}_i = |\boldsymbol{M}_i|\boldsymbol{s}_i$ are fixed, so that the directional unit vectors $\boldsymbol{s}_i$ (which we will call "spins" in the following) are the only degrees of freedom, hence $E_H = -\sum_{i<j}\tilde{J}_H(\boldsymbol{s}_i \cdot \boldsymbol{s}_j)$ with $\tilde{J}_H = J_H|\boldsymbol{M}_i||\boldsymbol{M}_j|$.

Simulations based on the nearest-neighbor Heisenberg model are certainly able to give a qualitative feeling for some aspects of nanoscale magnetism, but quantitatively E_H was observed to fail badly, as revealed by the *ab initio* electron theory.[13] For small relative spin cantings a bilinear expression of the form of Eq. (1) may indeed be valid, however, in general one has to go far beyond the nearest-neighbor approximation[9,10] (especially for Fe) and one has to take into account coupling constants J_{ij} which can depend very sensitively on the positions of the interacting atoms in the nanostructure.[11] For large noncollinearity, however, the bilinear form becomes completely unreliable.[13]. In this case the magnitudes of the magnetic moments $|\boldsymbol{M}_i|$ can depend strongly[13] on the spin configuration $\boldsymbol{\sigma} = (\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N)$ (especially for Ni), and from theoretical reasoning (based, e.g., on the Hubbard model) one has to take into account explicitly multispin interactions. In the past tentatively one or the other multispin interaction term has been added to the bilinear form of Eq. (1).[14] However, to the best knowledge of the authors no method exists that generalizes the bilinear Heisenberg model systematically.

In this paper we present a new method, the spin-cluster expansion (SCE) method, which represents a parametrization of the adiabatic magnetic energy surface including arbitrary complex multispin interactions on the atomic level. Thereby, the SCE is not limited to the dominant exchange interaction, but it includes also other spin interactions like the magnetic anisotropy, the dipolar and the Zeeman interaction. For a given system, all relevant parameters can be calculated by the *ab initio* electron theory. Once a numerically converged SCE expansion has been constructed, it yields the magnetic energy for any spin configuration with *ab initio* accuracy while being orders of magnitude faster than the *ab initio* electron theory for noncollinear spin systems. The SCE energy then can be used for an efficient dynamical or thermodynamical modeling of magnetic properties.

We termed our method SCE as it extends the cluster expansion method (CE) of alloy theory.[15] The CE allowed a systematic generalization of the Ising model in lattice systems and led to a unified approach to the calculation of phase diagrams. We are hopeful that the SCE developed in the present paper will have an equally strong impact.

Our theory is based on two major steps. In the first step we define the basic spin variables for the parametrization of the energy surface (Sec. II A). We use adiabatic spin variables, and therefore confine ourselves to situations for which the adiabatic approximation holds. The adiabatic approximation was successfully used in *ab initio* calculations of the ground states and of the spin dynamics in the recent past.[4–11] No attempt is made in the present paper to go beyond this approximation or to include the orbital magnetization. In the second step (Sec. II B) we present the parametrization of the general energy surface for the adiabatic spin variables. Former parametrizations of the energy surface were performed in terms of the cosines of the angles between spin vectors (“two-spin basis functions”). This is outlined, for instance, in Ref. 16, but to the best of our knowledge this kind of parametrization never has been worked out explicitly to the end, i.e., it has not been specified which of the various possible multispin terms survive in view of the symmetry restrictions. In the present paper we follow the strategy of the conventional cluster expansion for alloy systems[15] and use one-spin rather than two-spin basis functions for a representation of the adiabatic energy surface. The advantage of one-spin basis functions is that they allow to include systematically contributions to the magnetic energy which depend on the directions of the spins and not only on the angles between the spin vectors, for instance, the magnetic anisotropy and the Zeeman interaction. It is shown how a complete basis for the representation of the energy surface including arbitrarily high multispin interactions may be constructed from the one-spin basis functions. In Sec. II C the evaluation of the interaction parameters of the SCE is related to methods of the *ab initio* electron theory. In a practical calculation the SCE which represents an infinite sum of contributions from arbitrarily large spin clusters has to be terminated at a maximum cluster. It is argued that only a relatively small number of spin clusters is required to arrive at a terminated SCE which has *ab initio* accuracy, and it is demonstrated how the interaction parameters of this terminated SCE can be obtained from a relatively small number of *ab initio* calculations of the total energy of selected reference spin configurations. In Sec. II D it is shown how the spin clusters which have to be considered in the SCE can be extracted from the whole set of conceivable spin clusters by symmetry arguments. Finally, the relation is discussed between the one-spin representation of the SCE and the commonly used two-spin representation based on the cosines of the angles between the spin vectors, and this relation is worked out explicitly for pair interactions. An outlook is given in Sec. III.

II. DEVELOPMENT OF THE SPIN CLUSTER EXPANSION

A. Choice of adiabatic spin variables

The SCE allows to study the ground state properties of any magnetic system. For the application to dynamic and thermodynamic properties, the adiabatic approximation must hold, i.e., for the system under consideration the fast spin degrees of freedom from single-electron spin fluctuations on a time scale given by the inverse band width (typically 10^{-16} s) can be neglected and only slow degrees of freedom which describe the dynamics of the atomic moments $\boldsymbol{M}_i = |\boldsymbol{M}_i| \boldsymbol{s}_i$ on a time scale defined by the inverse frequencies of typical long-wavelength magnons (typically 10^{-14} s) are relevant. We thereby define the atomic moment in the common way as an integral of the magnetic moment density $\boldsymbol{m}(\boldsymbol{r})$ over a suitably defined atomic volume V_i,

$$\boldsymbol{M}_i = \int_{V_i} \boldsymbol{m} dV. \tag{2}$$

For dynamic and thermodynamic considerations we furthermore assume that the primary fluctuation modes of $\boldsymbol{M}_i$ are the transversal fluctuations given by the directional fluctuations of $\boldsymbol{s}_i$, whereas the magnitudes $|\boldsymbol{M}_i|$ are completely determined by the momentary spin configuration $\boldsymbol{\sigma}$. In contrast to the classical Heisenberg model we thus allow for longitudinal degrees of freedom, i.e., changes of the magnetic moments $|\boldsymbol{M}_i|$, but the longitudinal fluctuations are not independent but “slaved” by the transversal fluctuations. This condition is fulfilled by a very large class of materials but there are few exceptions (e.g., ZrZn_2).

The quantities $\boldsymbol{s}_i$ will be treated as classical variables in the following. Quantum mechanical effects on the time scale of the fast degrees of freedom will be included in the theory by calculating the magnetic moments $\boldsymbol{M}_i$ for given $\boldsymbol{s}_i$ via electron theory. Quantum mechanical effects on the slow time scale of the adiabatic variables $\boldsymbol{s}_i$ will be neglected totally. It should be noted that the adiabatic approximation which parametrizes the total energy completely in terms of the spin directions has been used successfully in the past to study the static and dynamical properties of the spin systems in solids.[4–11] For instance, exactly the same arguments for a parametrization in terms of spin directions were given by Gyorffy *et al.*[5] for a justification of their disordered local moment treatment of the ferromagnetic-paramagnetic transition.

B. Parametrization of the adiabatic energy surface

We now demonstrate in a mathematically rigorous manner how the adiabatic energy surface, including all relevant magnetic interactions in the solid (exchange energy, anisotropy energy, dipolar and Zeeman energy), may be represented exactly in terms of one-spin basis functions, i.e., basis functions which are associated so single spins $\boldsymbol{s}_i$ and not to the angles between the spin vectors as in a two-spin basis. The arguments represent a step-by-step generalization of the arguments given in the conventional cluster expansion for the case of a general Ising model.[15] Having obtained the energy surface it is possible to calculate the magnetic ground state configuration, the dynamical properties via an atomic Landau-Lifshitz-Gilbert equation or the thermodynamic properties via Monte Carlo simulations, for instance. In the paper of Gyorffy *et al.*[5] which is based on the same choice of the adiabatic spin variables $\boldsymbol{s}_i$ no attempt was made to obtain a general representation of the adiabatic energy surface, but the paper aimed at a variational mean field treatment of the statistical problem.

In spherical coordinates the spin is in general parametrized by two angles,

$$\boldsymbol{s}_i = \boldsymbol{s}_i(\boldsymbol{\Omega}) = \boldsymbol{s}_i(\vartheta, \varphi), \tag{3}$$

with $\vartheta \in [0,\pi]$ and $\varphi \in [0,2\pi)$. Special cases are the $x-y$ model where the spin is confined to a plane ($\vartheta = \pi/2$) and the Ising model where only two spin states, $\vartheta = 0$ and $\vartheta = \pi$ are possible. The connection to alloy theory[15] is made by allowing angles $\vartheta = p\pi/(P-1)(\varphi = 0)$, with $p = 0, \ldots, P-1$ in a P-component alloy. By imposing suitable constraints on the spin directions, we can calculate, e.g., by the spin-density functional electron theory the energy of a magnetic system of atoms as a function of the spin directions,

$$E^{(0)}(\boldsymbol{\sigma})=E^{(0)}(\boldsymbol{s}_1,\boldsymbol{s}_2,\ldots,\boldsymbol{s}_N). \tag{4}$$

When the electron theory includes the spin-orbit coupling then the magnetic energy encompasses the exchange energy and the magnetic anisotropy energy. Because we can calculate in addition from the magnetization density $\boldsymbol{m}(\boldsymbol{r})$ provided by the electron theory all magnetic moments $\boldsymbol{M}_i$ we also can add the dipolar interaction energy of the magnetic moments $\boldsymbol{M}_i$. For the moment we exclude the Zeeman interaction energy which requires a separate treatment (see below) and denote the sum of the exchange, anisotropy and dipolar energy as contribution $E^{(0)}$ to the magnetic energy.

We next develop the SCE formalism that allows us to expand systematically the magnetic energy $E^{(0)}(\boldsymbol{s}_1,\boldsymbol{s}_2,\ldots,\boldsymbol{s}_N)$. We define the scalar product in the N-spin system in terms of functions associated to the single spins $\boldsymbol{s}_i$,

$$\langle f|g\rangle=\mathrm{Tr}^{(N)}f^{*}\cdot g, \tag{5}$$

where $f(\boldsymbol{s}_1,\ldots,\boldsymbol{s}_N)$ and $g(\boldsymbol{s}_1,\ldots,\boldsymbol{s}_N)$ are functions of the spin directions and the trace is defined as

$$\mathrm{Tr}^{(N)}=\frac{1}{\Theta^N}\int d\Omega_1\int d\Omega_2\ldots\int d\Omega_N, \tag{6}$$

with $\Theta=\int d\Omega$ for the case of a continuous spin symmetry (general case and x-y model). For the Ising model the integrations have to be replaced by summations over the two possible orientations. Next we introduce a set of orthogonal and complete one-spin basis functions $\phi_\upsilon(\boldsymbol{s}),\upsilon=0,\ldots,\infty$, that are attached to every spin site,

$$\frac{1}{\Theta}\int d\Omega\,\phi^{*}_{\upsilon_1}(\boldsymbol{s})\phi_{\upsilon_2}(\boldsymbol{s})=\delta_{\upsilon_1\upsilon_2}, \tag{7}$$

$$\frac{1}{\Theta}\sum_{\upsilon=0}^{\infty}\phi^{*}_{\upsilon}(\boldsymbol{s}_1)\phi_\upsilon(\boldsymbol{s}_2)=\delta(\boldsymbol{s}_1-\boldsymbol{s}_2). \tag{8}$$

By demanding $\phi_0(\boldsymbol{s})=1$, we get for $i\neq j$,

$$\begin{aligned}\langle\phi_{\upsilon_1}(\boldsymbol{s}_i)|\phi_{\upsilon_2}(\boldsymbol{s}_j)\rangle&=\langle\phi_{\upsilon_1}(\boldsymbol{s}_i)\phi_0(\boldsymbol{s}_j)|\phi_0(\boldsymbol{s}_i)\phi_{\upsilon_2}(\boldsymbol{s}_j)\rangle\\&\overset{\text{Eq. (7)}}{=}\delta_{\upsilon_1 0}\delta_{0\upsilon_2},\end{aligned} \tag{9}$$

while for identical spin sites $i=j$ we find

$$\langle\phi_{\upsilon_1}(\boldsymbol{s}_i)|\phi_{\upsilon_2}(\boldsymbol{s}_i)\rangle\overset{\text{Eq. (7)}}{=}\delta_{\upsilon_1\upsilon_2}. \tag{10}$$

For $\upsilon_1\neq 0,\upsilon_2\neq 0$, Eqs. (9), (10) are combined into

$$\langle\phi_{\upsilon_1}(\boldsymbol{s}_i)|\phi_{\upsilon_2}(\boldsymbol{s}_j)\rangle=\delta_{\upsilon_1\upsilon_2}\delta_{ij}. \tag{11}$$

For example, one-spin basis functions for the general case are the spherical harmonics $Y_{lm}(\vartheta,\varphi)$ (see below), for the $x-y$ model the exponentials $\exp(\imath n\varphi)$ where n is an integer number, and for the Ising model we can take $\phi_1(s)=s$ with $s=\pm 1$. In the latter case the SCE attains the same form as the CE of a binary alloy.

The basis functions of the full N-spin system are formally constructed from products of one-spin basis functions,

$$\Phi_{\tilde{\alpha}\tilde{\nu}}=\phi_{\upsilon_1}(\boldsymbol{s}_{i_1})\phi_{\upsilon_2}(\boldsymbol{s}_{i_2})\ldots\phi_{\upsilon_N}(\boldsymbol{s}_{i_N}), \tag{12}$$

where the cluster $\tilde{\alpha}=\{i_1,i_2,\ldots i_N\}$ contains all sites of the N-spin system and $\tilde{\nu}=(\upsilon_1,\upsilon_2,\ldots,\upsilon_N)$ labels the corresponding one-spin basis functions. The complete set of basis functions is obtained by summing over all possible values of the one-spin basis functions contained in $\tilde{\nu}$. The basis functions of the N-spin system are orthogonal and complete,

$$\langle\Phi_{\tilde{\alpha}\tilde{\nu}}|\Phi_{\tilde{\beta}\tilde{\mu}}\rangle=\delta_{\tilde{\alpha}\tilde{\beta}}\delta_{\tilde{\nu}\tilde{\mu}} \tag{13}$$

$$\frac{1}{\Theta^N}\sum_{\tilde{\nu}}\Phi^{*}_{\tilde{\alpha}\tilde{\nu}}(\boldsymbol{\sigma})\Phi_{\tilde{\alpha}\tilde{\nu}}(\boldsymbol{\sigma}')=\delta(\boldsymbol{\sigma}-\boldsymbol{\sigma}'). \tag{14}$$

The choice $\phi_0(\boldsymbol{s})=1$ allows us to recast the N-spin basis in order to allow a local interpretation of the spin-cluster expansion in total analogy to the procedure adopted in the conventional cluster expansion[15] for generalized Ising models. Let us look, for example, at one special N-spin basis function $\Phi_{\tilde{\alpha}\tilde{\nu}}$ with $\upsilon_l=0$ $(1\leqslant l\leqslant N)$. Taking into account $\phi_0(\boldsymbol{s}_l)=1$, the basis function $\Phi_{\tilde{\alpha}\tilde{\nu}}$ equals a basis function $\Phi_{\tilde{\beta}\tilde{\mu}}$ of a $(N-1)$-spin system without the spin site i_l, $\tilde{\beta}=\{i_1,i_2,\ldots,i_{l-1},i_{l+1},\ldots,i_N\}$ and $\tilde{\mu}=(\upsilon_1,\upsilon_2,\ldots,\upsilon_{l-1},\upsilon_{l+1},\ldots,\upsilon_N)$. Hence we can formally replace all N-spin basis functions that contain L (with $0\leqslant L\leqslant N$) products of the basis function ϕ_0 by their corresponding basis functions in a $(N-L)$-spin system. Basis functions that have been reduced so that $\tilde{\mu}=(\upsilon_1,\upsilon_2,\ldots,\upsilon_N)$ contains only elements $\upsilon_l\neq 0$ are now denoted by

$$\Phi_{\alpha\nu}=\phi_{\upsilon_1}(\boldsymbol{s}_{i_1})\phi_{\upsilon_2}(\boldsymbol{s}_{i_2})\ldots\phi_{\upsilon_K}(\boldsymbol{s}_{i_K}), \tag{15}$$

where in contrast to Eq. (12) the cluster α now can contain any number $K=0,\ldots,N$ of spin sites. The one-spin basis functions in the cluster α, denoted by $\nu=(\upsilon_1,\upsilon_2,\ldots,\upsilon_K)$ now are all different from zero, $\upsilon_l\neq 0$, with $1\leqslant l\leqslant K$. This allows to rewrite the orthogonality and completeness relation Eqs. (13) and (14) using Eq. (11),

$$\langle\Phi_{\alpha\nu}|\Phi_{\beta\mu}\rangle=\delta_{\alpha\beta}\delta_{\nu\mu}, \tag{16}$$

$$\frac{1}{\Theta^K}\left(1+\sum_{\gamma\subseteq\alpha}\sum_{\nu}\Phi^{*}_{\gamma\nu}(\boldsymbol{\sigma})\Phi_{\gamma\nu}(\boldsymbol{\sigma}')\right)=\delta(\boldsymbol{\sigma}-\boldsymbol{\sigma}'), \tag{17}$$

where the sum over ν runs over all one-spin basis functions except $\phi_0=1$ of the sites in the subcluster γ of an arbitrary cluster $\alpha=\{i_1,\ldots,i_K\}$, and $\boldsymbol{\sigma}$, $\boldsymbol{\sigma}'$ denote spin configurations of the cluster α, and $\delta(\boldsymbol{\sigma}-\boldsymbol{\sigma}')=\delta(\boldsymbol{s}_{i_1}-\boldsymbol{s}'_{i_1})\ldots\delta(\boldsymbol{s}_{i_K}-\boldsymbol{s}'_{i_K})$. The zero cluster function is given by $\Phi_0=1$. A spin dependent function, e.g., $E^{(0)}(\boldsymbol{s}_1,\boldsymbol{s}_2,\ldots,\boldsymbol{s}_N)$ can be expressed in this basis,

$$E^{(0)}(\boldsymbol{\sigma})=J_0+\sum_{\alpha}\sum_{\nu}J_{\alpha\nu}\Phi_{\alpha\nu}(\boldsymbol{\sigma}), \tag{18}$$

where the expansion coefficients according to Eq. (16) are given by

$$J_{\alpha\nu} = \langle \Phi_{\alpha\nu} | E^{(0)}(\boldsymbol{\sigma}) \rangle . \tag{19}$$

The expansion coefficients thereby are constant, independent of the spin configuration $\boldsymbol{\sigma} = (\boldsymbol{s}_1, \ldots, \boldsymbol{s}_N)$. As the expansion coefficients depend only on a local subcluster α with $K < N$ sites, the interpretation of the expansion coefficients $J_{\alpha\nu}$ is straightforward.

J_0: Constant energy offset, independent of spin directions.

$J_{\{i\}\nu}$: The point cluster expansion coefficients describe the energy required to rotate a spin at site i irrespective of the spin directions of the other spins. These expansion coefficients are thus closely related to the magnetic anisotropy. Also, they contain the coupling to an external magnetic field in lowest approximation (see below).

$J_{\{i,j\}\nu}$: The pair cluster expansion coefficient describes the coupling of two spins at sites i,j.

The contribution of the Zeeman interaction energy,

$$E^{Zeeman} = -\boldsymbol{H} \cdot \boldsymbol{M}_{tot} = -\boldsymbol{H} \cdot \sum_{i=1}^{N} |\boldsymbol{M}_i| \boldsymbol{s}_i , \tag{20}$$

requires a separate consideration because a magnetic field can change in principle the magnitudes $|\boldsymbol{M}_i|$ even for fixed spin configuration $\boldsymbol{\sigma}$, i.e., $\boldsymbol{M}_{tot} = \boldsymbol{M}_{tot}(\boldsymbol{H},\boldsymbol{\sigma})$. In principle we could calculate *ab initio* $\boldsymbol{M}_{tot}(\boldsymbol{H},\boldsymbol{\sigma})$ for various magnetic fields $\boldsymbol{H}$, add the Zeeman energy to $E^{(0)}$ and perform a SCE for the sum $E^{mag} = E^{(0)} + E^{Zeeman}$, arriving at field dependent expansion coefficients $J_{\alpha\nu} = J_{\alpha\nu}(\boldsymbol{H})$. For many systems, however, the magnitudes $|\boldsymbol{M}_i|$ of the magnetic moments at a given spin configuration $\boldsymbol{\sigma}$ do not depend on the magnetic field $\boldsymbol{H}$ for moderate applied fields. In the following we thus neglect the explicit dependence of the total magnetic moment on the magnetic field, i.e., we assume $\boldsymbol{M}_{tot} = \boldsymbol{M}_{tot}(\boldsymbol{\sigma})$. Then we can perform a SCE of $\boldsymbol{M}_{tot}$ arriving at an expression for the total magnetic energy of the form

$$E^{mag} = E^{(0)}(\boldsymbol{\sigma}) - \boldsymbol{H} \cdot \boldsymbol{M}_{tot}(\boldsymbol{\sigma}). \tag{21}$$

If furthermore the magnitude of the magnetic moments $|\boldsymbol{M}_i|$ does not depend on $\boldsymbol{\sigma}$, then the Zeeman energy contributes only to the point cluster expansion coefficient of the SCE. It should be recalled that thus the present method incorporates all the magnetic interactions, i.e., exchange interactions, anisotropy energy, dipolar and Zeeman energy in one and the same scheme, the spin-cluster expansion, and we think that this is a big advantage of our approach.

C. Practical realization of an *ab initio* SCE

In practice, an *ab initio* SCE is constructed in the following way. First we define the positions of the atoms in the system under consideration. If these are the positions of a regular lattice then the spin clusters appearing in Eq. (18) can be grouped together in classes of symmetry equivalent clusters.[15] The number of nonequivalent clusters increases when the translational symmetry is broken, e.g., at surfaces[17] and especially for small clusters. Second, it must be recalled that the SCE, Eq. (18), represents an infinite sum over contributions arising from infinitely many spin cluster figures (labeled by α) and from infinitely many one-spin basis functions (labeled by ν) for each site (in the case of a continuous spin symmetry). To evaluate the infinitely many corresponding expansion coefficients $J_{\alpha\nu}$ via the projection operation given by Eq. (19) would require the knowledge of the complete energy surface $E^{(0)}(\boldsymbol{\sigma})$ in the infinitely dimensional configuration space. It is totally clear that for a practical approach the series Eq. (18) has to be terminated with respect to the number and type of clusters which are taken into account (as in the conventional CE) and with respect to the number of considered single spin basis functions in the case of systems with continuous spin symmetry (whereas in the conventional CE for P-component alloys all P basis functions are kept). For the determination of the remaining n_1 expansion coefficients $J_{\alpha\nu}$ we proceed exactly in the same way as in the conventional cluster expansion for alloy systems.[15] A set of $n_2 \geqslant n_1$ appropriately chosen (see below) reference configurations $\boldsymbol{\sigma}_{ref}$ is defined, and then the energy $E^{(0)}(\boldsymbol{\sigma}_{ref})$ is calculated by the *ab initio* electron theory, for instance, with the computational techniques described in Refs. 4–11. Then the n_1 coefficients $J_{\alpha\nu}$ are calculated by fitting the terminated SCE series to the n_2 energies[18,19] $E^{(0)}(\boldsymbol{\sigma}_{ref})$. Finally, the terminated SCE must be tested for numerical convergence with respect to the number and type of considered clusters (see also Sec. II D) and one-spin basis functions, and for this test the sophisticated techniques derived for the conventional CE (for a review, see Ref. 20) can be used. A numerically converged *ab initio* SCE is obtained if the error due to the termination of the series is smaller than the numerical error involved in the *ab initio* calculations themselves. We assume that (similar to the case of the CE) the SCE converges rather rapidly.

It should be noted that the degree of convergence depends also on the type of chosen reference configurations. As in the conventional CE, there is no strict prescription how to choose these configurations, it is more a matter of physical intuition and of trial and error. Of course the reference configurations will be chosen in such a way that they are representative for the situation under consideration, i.e., no configuration will be chosen which appears in that situation only with negligible weight.

D. Symmetry arguments and relation to the classical Heisenberg model

Symmetry considerations can greatly help to reduce the number of clusters that have to be considered in the SCE. First, time reversal symmetry implies

$$E(\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N) = E(-\boldsymbol{s}_1, -\boldsymbol{s}_2, \ldots, -\boldsymbol{s}_N). \tag{22}$$

In practice, this requirement leads to linear dependencies between the expansion coefficients $J_{\alpha\nu}$. Hence, it is useful to choose the one-spin basis functions ϕ_v such that they have a simple transformation behavior with respect to inversion of the spin directions. Furthermore, in many systems the spin-orbit coupling (SOC) energy is small compared to the coupling between the magnetic moments on different lattice sites. In what follows we treat the important special case of zero SOC energy. Then the energy of the electronic system is invariant with respect to rotations $\boldsymbol{R}$ of the magnetic moment density,

$$E[\boldsymbol{m}]=E[\boldsymbol{R}:\boldsymbol{m}]. \tag{23}$$

According to the definition of the magnetic moment $\boldsymbol{M}_i$, Eq. (2), the rotational invariance of Eq. (23) translates into

$$E(\boldsymbol{s}_1,\boldsymbol{s}_2,\ldots,\boldsymbol{s}_N)=E(\boldsymbol{R}:\boldsymbol{s}_1,\boldsymbol{R}:\boldsymbol{s}_2,\ldots,\boldsymbol{R}:\boldsymbol{s}_N). \tag{24}$$

Hence, the energy is invariant with respect to group elements of the inversion group C_i and rotations from $SO(3)$, $O(3)=SO(3)\times C_i$. This invariance leads to linear dependencies between the expansion coefficients $J_{\alpha\nu}$ which are best subsumed if the one-spin basis forms an irreducible basis of the point group under consideration, namely spherical harmonics Y_{lm}[21] for the group $O(3)$. In order to have $\phi_0=y_{00}=1$ we multiply the spherical harmonics by a factor $\sqrt{4\pi}$,

$$y_{lm}=\sqrt{4\pi}Y_{lm}. \tag{25}$$

Spherical harmonics form an orthogonal and complete basis set,

$$\frac{1}{4\pi}\int d\Omega y^*_{l_1m_1}(\Omega)y_{l_2m_2}(\Omega)=\delta_{l_1l_2}\delta_{m_1m_2}, \tag{26}$$

$$\frac{1}{4\pi}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}y^*_{lm}(\Omega_1)y_{lm}(\Omega_2)=\delta(\Omega_1-\Omega_2), \tag{27}$$

with $\delta(\Omega_1-\Omega_2)=\delta(\cos\vartheta_1-\cos\vartheta_2)\delta(\varphi_1-\varphi_2)$. From the SCE representation of the energy Eq. (18) it follows that only linear combinations of the cluster basis functions contribute to $E(\boldsymbol{\sigma})$ that are invariant with respect to point group operations $\boldsymbol{R}\in O(3)$. Hence, we need to find the irreducible representations $D^{(0)}$ that are invariant with respect to group operations from $O(3)$ that are contained in the products of spherical harmonics.

Obviously none of the one-spin basis functions is invariant with respect to rotations for $\nu\neq 0$ (according to $l\neq 0$ for spherical harmonics), hence,

$$J_{\{i\}\nu}=0. \tag{28}$$

For pair cluster expansion coefficients the product of two representations is evaluated. With

$$D^{(l_1)}\times D^{(l_2)}=\sum_{L=|l_1-l_2|}^{l_1+l_2}D^{(L)}, \tag{29}$$

for the special case $\boldsymbol{s}_1=\boldsymbol{s}_2$ we see that only basis functions with $l=l_1=l_2$ contribute to the SCE as the total energy has to be invariant with respect to point group operations $\boldsymbol{R}\in O(3)$ and thus only irreducible representations $D^{(0)}$ formed by the product of two sets of one-spin basis functions contribute to the energy. The corresponding pair cluster basis function is calculated from spherical harmonics as[21]

$$\Phi_{\{ij\}(ll)}(\boldsymbol{s}_i,\boldsymbol{s}_j)=\sum_{m=-l}^{l}y^*_{lm}(\Omega_i)y_{lm}(\Omega_j)=(2l+1)P_l(\boldsymbol{s}_i\cdot\boldsymbol{s}_j), \tag{30}$$

with the Legendre polynomials P_l.[21] Thus, the contribution of pair clusters to the energy can be written as

$$E^{(2)}=\sum_l\sum_{i<j}J_{\{ij\}(ll)}(2l+1)P_l(\boldsymbol{s}_i\cdot\boldsymbol{s}_j). \tag{31}$$

In lowest order $l=1$ the pair contribution reduces to the Heisenberg model,

$$E_H=-\sum_{i<j}\tilde{J}_H(\boldsymbol{s}_i\cdot\boldsymbol{s}_j),\quad \tilde{J}_H=-3J_{\{ij\}\{11\}}. \tag{32}$$

Obviously, Eq. (31) is the most general form of an exchange Hamiltonian which contains two-spin interactions of the form $(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)$. We thereby gained the relation between the expansion coefficients $J_{\{ij\}(11)}$ of the SCE expansion in the one-spin basis functions and the coefficients $\tilde{J}_H$ of the representation in the two-spin cosine basis.

Generalizations of the Heisenberg model[14] suggest that also multispin interactions can be parametrized by products $(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)$. By using the relation[22]

$$(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)=\frac{1}{3}\sum_{m=-1}^{1}y^*_{1m}(\Omega_i)y_{1m}(\Omega_j), \tag{33}$$

these products can be represented according to a spin-cluster expansion with spherical harmonics as one-spin basis functions. It would be most interesting to find out if the inverse also holds, i.e., if the SCE in general can be mapped on multispin products of the form $(\boldsymbol{s}_i\cdot\boldsymbol{s}_j)$.

III. OUTLOOK

We are in the process of constructing a well converged SCE first for the case of bulk Fe and Co. As the general multispin interactions provided by the SCE method to the best knowledge of the authors have never been evaluated elsewhere, it will be most interesting to determine the actual contribution of non-Heisenberg interactions in Fe and Co. Our efforts are planned to cumulate in a systematic, fully *ab initio* based treatment of small clusters of Fe and Co. The understanding and modeling of the properties of such clusters is of great relevance for the design of magnetic nanoscale devices.

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