Non-collinear Korringa-Kohn-Rostoker Green function method: Application to 3d nanostructures on Ni(001)

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Magnetic nanostructures on non-magnetic or magnetic substrates have attracted strong attention due to the development of new experimental methods with atomic resolution. Motivated by this progress we have extended the full-potential Korringa-Kohn-Rostoker (KKR) Green function method to treat non-collinear magnetic nanostructures on surfaces. We focus on magnetic 3d impurity nanoclusters, sitting as adatoms on or in the first surface layer on Ni(001), and investigate the size and orientation of the local moments and moreover the stabilization of non-collinear magnetic solutions. While clusters of Fe, Co, Ni atoms are magnetically collinear, non-collinear magnetic coupling is expected for Cr and Mn clusters on surfaces of elemental ferromagnets. The origin of frustration is the competition of the antiferromagnetic exchange coupling among the Cr or Mn atoms with the antiferromagnetic (for Cr) or ferromagnetic (for Mn) exchange coupling between the impurities and the substrate. We find that Cr and Mn first-neighbouring dimers and a Mn trimer on Ni(001) show non-collinear behavior nearly degenerate with the most stable collinear configuration. Increasing the distance between the dimer atoms leads to a collinear behavior, similar to the one of the single impurities. Finally, we compare some of the non-collinear ab-initio results to those obtained within a classical Heisenberg model, where the exchange constants are fitted to total energies of the collinear states; the agreement is surprisingly good.

I. INTRODUCTION

Theoretically, extensive work is carried out in the area of complex non-collinear magnetism, particularly for surface and bulk systems. In fact a lot of interesting physics would be missed if only collinear magnetic structures were considered. In fact, magnetic nanostructures on magnetic or non-magnetic substrates are attractive to the scientific community due to their novel and unusual properties, being of relevance both for theory as well as for the applications in the magneto-electronics devices.

One of these properties is the non-collinear magnetic order occurring for geometrically frustrated antiferromagnets, e.g. on a triangular lattice, in disordered systems, exchange bias systems, and molecular magnets, or for systems which exhibit either competing exchange interactions, or between exchange and spin-orbit interactions. A simple model for frustration is the following: Starting with an antiferromagnetic (AF) Cr dimer, the addition a third Cr atom to form an equilateral triangle leads to a frustrated geometry. Each atom would like to couple AF to both other atoms. Since this is impossible, the moments of the three atoms rotate until a compromise is found. The ground state is then non-collinear, characterized by an angle of 120° between each two atoms. The same situation will also occur for the AF Cr dimer, since the interaction of both Cr atoms with the ferromagnetic substrate atoms is either ferromagnetic or antiferromagnetic. As we will show in this paper, also in this case a non-collinear structure can result.

The majority of the ab-initio methods available for the treatment of non-collinear magnetism make explicit use of Bloch’s theorem and are thus restricted to periodic systems (bulk or films). Then, even for collinear magnetism, one needs huge supercells to simulate impurities in a given host (bulk or film) in order to avoid spurious interactions of the impurities from adjacent supercells. A few methods have been developed to treat free clusters, but to our knowledge no ab-initio methods exist for the investigation of non-collinear magnetism of clusters in bulk or deposited on surfaces.

First non-collinear calculations by the KKR Green function method, though not self-consistent, were already performed in 1985. Oswald et al.16 could show by using the method of constraints that the exchange interaction between the moments of Mn and Fe impurity pairs in Cu is in good approximation described by the \( \cos \theta \)-dependence of the Heisenberg model.

Sandratskii et al.17 and Kübler et al.18 pioneered the investigation of non-collinear magnetic structures using self-consistent density functional theory. One of the first systems studied by Sandratskii et al. was the spin spiral of bcc Fe with the KKR method. Later on, \( \Delta \)-Fe was a hot topic, and the appearance of the experimental work of Tsunoda et al.9,10 led to the development of other first-principles methods able to deal with non-collinear magnetism such as LMTO11, ASW12 and FLAPW13,14,15.

Several papers16,17 describe how symmetry simplifies the calculational effort for the spiral magnetic structures in the case of perfect periodic systems—this involves the generalized Bloch theorem. In ab-initio methods, this principle is used together with the constrained density functional theory18,19 giving the opportunity of studying arbitrary magnetic configurations where the orientations of the local moments are constrained to nonequilibrium directions.

Concerning free clusters, few methods are developed. For example, Oda et al.20 developed a plane-wave pseudopotential scheme for non-collinear magnetic structures. They applied it to small Fe clusters for which they found...
non-collinear magnetic structures for Fe₃ and linear-shape Fe₂. This last result was in contradiction with the work of Hobbs et al. who found only a collinear ferromagnetic configuration using a projector augmented-wave method. Small Cr clusters were found magnetically non-collinear as shown also by Kohl and Bertsch using a relativistic nonlocal pseudopotential method after optimization of the ionic structure by a Monte Carlo technique. However, within the generalized gradient approximation (GGA) of density-functional theory, Hobbs et al. find that in many cases the non-collinear states can be metastable, while the ground-state solutions are collinear and arise after geometrical optimization of the free-standing clusters.

One main result of Oda et al. and Hobbs et al. concerns the variation of the magnetization density with the position. The spin direction changes in the interstitial region between the atoms where the charge and magnetization densities are small, while the magnetization is practically collinear within the atomic spheres. This supports the use of a single spin direction for each atomic sphere as an approximation in order to accelerate the computation; this approximation is followed also here.

The aim of this work is to present a method based on the full-potential KKR scheme which can deal with non-collinear magnetism in systems of reduced symmetry. This method is ideal for treating impurities or small clusters on surfaces or in bulk. As an application we study small 3d clusters on the Ni(001) surface where we find complex magnetic configurations.

## II. NON-COLLINEAR KKR FORMALISM

The KKR method uses multiple-scattering theory in order to determine the one-electron Green function in a mixed site and angular–momentum representation. The retarded Green function is expanded as:

\[
G(\vec{R}_n + \vec{r}, \vec{R}_n' + \vec{r}'; E) = -i\sqrt{E} \sum_L R_L^\sigma(\vec{r}_<; E)H_L^\delta(\vec{r}_>; E)\delta_{nn'} + \sum_{LL'} R_L^\sigma(\vec{r}; E)G_{LL'}^{nn'}(E)R_{L'}^{\delta}(\vec{r}'; E) \tag{1}
\]

Here, \(E\) is the energy and \(\vec{R}_n\), \(\vec{R}_n'\) refer to the atomic nuclei positions. By \(\vec{r}_<\) and \(\vec{r}_>\) we denote respectively the shorter and longer of the vectors \(\vec{r}\) and \(\vec{r}'\) which define the position in each Wigner–Seitz cell relative to the position \(\vec{R}_n\) or \(\vec{R}_n'\). The wavefunctions \(R_L^\sigma(\vec{r}; E)\) and \(H_L^\delta(\vec{r}; E)\) are, respectively, the regular and irregular solutions of the Schrödinger equation for the potential \(V_n\) at site \(n\), being embedded in free space; \(L = (l, m)\) is a combined index for angular momentum quantum numbers; \(l\) is truncated at a maximum value of \(l_{\text{max}}\). The first term on the LHS of Equation (1) is the so-called single site scattering term, which describes the behavior of an atom \(n\) in free space. All multiple- and back-scattering information is contained in the second back-scattering term via the structural Green functions \(G_{LL'}^{nn'}(E)\) which are obtained by solving the algebraic Dyson equation:

\[
G_{LL'}^{nn'}(E) = \delta_{LL'}^{nn'}(E) + \sum_{n''L''L'''} G_{LL''}^{nn''}(E)\Delta t_L^\sigma(\vec{r}, \vec{r}'; E)G_{L''L'}^{n'n''}(E) \tag{2}
\]

Equation (2) follows directly from the usual Dyson eq. of the form \(G = \hat{\sigma} + \hat{\sigma} \Delta V \hat{G}\), with \(\Delta V\) the perturbation in the potential and \(\hat{\sigma}\) the reference system Green function. The summation in (2) is over all lattice sites \(n''\) and angular momenta \(L''\) for which the perturbation \(\Delta t_L^\sigma(\vec{r}, \vec{r}'; E) = t_L^\sigma(\vec{r}, \vec{r}'; E) - \delta_{LL'}^{nn'}(E)\) between the \(t\) matrices of the real and the reference system is significant (the \(t\)-matrix gives the scattering amplitude of the atomic potential). The quantities \(\hat{\sigma}G_{LL'}^{nn'}(E)\) are the structural Green functions of the reference system. For the calculation of a crystal bulk or surface, the reference system can be free space, or, within the tight-binding KKR formulation a system of periodically arrayed repulsive potentials. After the host (bulk or surface) Green function is found, it can be used in a second step as a reference for the calculation of the Green function of an impurity or a cluster of impurities embedded in the host.

The algebraic Dyson equation (2) is solved by matrix inversion, as we will see later on in Equation (17). In case of spin-dependent electronic structure, spin indexes enter in the \(t\)-matrix, the Green functions and in Eq. (2). Especially in the case of non-collinear magnetism, these quantities become \(2 \times 2\) matrices in spin space, denoted by \(\mathbf{t}\) and \(\mathbf{G}\).

Once the spin-dependent Green function is known, all physical properties can be derived from it. In particular, the charge density \(n(\vec{r})\) and spin density \(\vec{m}(\vec{r})\) are given by an integration of the imaginary part of \(\mathbf{G}\) up to the Fermi level \(E_F\) and a trace over spin indexes \(s\) (putting the Green function in a matrix form in spin space):

\[
n(\vec{r}) = -\frac{1}{\pi} \text{ImTr}_s \int_{E_F}^{\infty} \mathbf{G}(\vec{r}, \vec{r}; E) dE \tag{3}
\]

\[
\vec{m}(\vec{r}) = -\frac{1}{\pi} \text{ImTr}_s \int_{E_F}^{\infty} \mathbf{\hat{G}}(\vec{r}, \vec{r}; E) dE. \tag{4}
\]
Here, $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices and $\text{Tr}_n$ means the trace operation in spin space.

The basic difference between non-collinear and collinear magnetism is the absence of a natural spin quantization axis common to the whole crystal. The density matrix is not anymore diagonal in spin space as in the case of collinear magnetism. Instead, in any fixed frame of reference it has the form

$$
\rho(\vec{r}) = \begin{bmatrix}
\rho_{\uparrow\uparrow}(\vec{r}) & \rho_{\uparrow\downarrow}(\vec{r}) \\
\rho_{\downarrow\uparrow}(\vec{r}) & \rho_{\downarrow\downarrow}(\vec{r})
\end{bmatrix} = \frac{1}{2} \left[ n(\vec{r}) + \vec{\sigma} \cdot \vec{m}(\vec{r}) \right]
$$

(5)

At any particular point in space, of course, a local frame of reference can be found in which $\rho$ is diagonal, but this local frame can change from point to point.

In order to deal with non-collinear magnetism, we have to solve the appropriate Dyson equation. First we define the reference system which is a perfect surface characterized by collinear magnetism. Although the collinearity of the reference system is not necessary, it serves our purpose of calculating the electronic structure of the ferromagnetic or nonmagnetic surfaces which are used as reference systems. Thus the host Green functions $\hat{G}$ and $t$-matrices $\hat{t}$ are assumed diagonal in spin space. In this way, in the case of a magnetic host, a global spin frame of reference is defined. The host $\hat{G}$ and $\hat{t}$ are thus of the form:

$$
\hat{G}(E) = \begin{bmatrix}
\hat{G}_{\uparrow\uparrow}(E) & 0 \\
0 & \hat{G}_{\downarrow\downarrow}(E)
\end{bmatrix}; \hat{t}(E) = \begin{bmatrix}
\hat{t}_{\uparrow\uparrow}(E) & 0 \\
0 & \hat{t}_{\downarrow\downarrow}(E)
\end{bmatrix}
$$

(6)

Then the perturbed system is constructed. The impurity atoms which might couple magnetically in a non-collinear way reside on the surface, perturbing the potential at a few neighboring sites (atoms or empty cells representing the potential in the vacuum). With this finite cluster of perturbed sites the magnetization can be non-collinear leading to the appearance of non-diagonal elements of the $t$-matrix:

$$
\hat{t}(E) = \begin{bmatrix}
\hat{t}_{\uparrow\uparrow}(E) & \hat{t}_{\uparrow\downarrow}(E) \\
\hat{t}_{\downarrow\uparrow}(E) & \hat{t}_{\downarrow\downarrow}(E)
\end{bmatrix}
$$

(7)

The non-diagonal $t$-matrix contains the information on spin-flip scattering by the atomic potential.

At this stage an approximation enters our method. It is assumed that, separately for each atom, there exists an intra-atomic spin quantization axis common to the whole atomic cell. This axis is identified with the spatial average of the magnetization density $\vec{m}_n(\vec{r})$ in each cell $n$. This defines the local spin frame of reference. In this way we neglect the variation of the spin quantization axis within the cell during self-consistency, avoiding the time-consuming numerical solution of the potential of coupled Schrödinger equations of the two spin channels. Within the local density approximation of density-functional theory, the exchange correlation potential has the same reference frame as the local magnetization $\vec{m}_n(\vec{r})$. Then for each atom we have a potential which is collinear in the local frame, and the solutions of the Schrödinger equation, $R_{nLs}^{loc}(\vec{r}; E)$ and $H_{nLs}^{loc}(\vec{r}; E)$, depending on the spin index $s$ of the local frame.

The solution of the Schrödinger equation separately for each spin channel provides also the diagonal $t$-matrix of each atomic cell $n$ in the local frame of reference:

$$
t_{n}^{\text{loc}}(E) = \begin{bmatrix}
t_{nL\uparrow\uparrow}^{\text{loc}}(E) & 0 \\
0 & t_{nL\downarrow\downarrow}^{\text{loc}}(E)
\end{bmatrix}
$$

(8)

Then the $t$-matrix is rotated from the local to the global spin frame of reference using the spin rotation matrix $U_n$:

$$
t_{n}^{\text{glob}}(E) = U_n t_{n}^{\text{loc}}(E) U_n^\dagger,
$$

(9)

$U_n$ being given by

$$
U_n = \begin{bmatrix}
\cos(\frac{\theta_n}{2})e^{-i\frac{\phi_n}{2}} & -\sin(\frac{\theta_n}{2})e^{i\frac{\phi_n}{2}} \\
\sin(\frac{\theta_n}{2})e^{i\frac{\phi_n}{2}} & \cos(\frac{\theta_n}{2})e^{-i\frac{\phi_n}{2}}
\end{bmatrix}.
$$

(10)

The polar angles $\theta_n$ and $\phi_n$ define the direction of the local magnetic moment with respect to the global spin frame of reference. Normally, $\theta_n$ and $\phi_n$ vary within the atomic cell, but in the approximation used here, average angles are defined for each cell via an averaging of the magnetization density within the cell. Of course, when self-consistency is achieved, both the averaged and the point-by-point varying magnetization direction can be extracted from the output density matrix. Thus the assumption of a unique spin direction in each cell is only made for the spin-dependent potential.

The $t$-matrix in the global spin frame of reference can be rewritten in the following way:

$$
t_{n}^{\text{glob}}(E) = U_n \left[ \frac{1}{2} (t_{nL\uparrow\uparrow}^{\text{loc}}(E) + t_{nL\downarrow\downarrow}^{\text{loc}}(E)) \mathbf{1} + \frac{1}{2} (t_{nL\uparrow\uparrow}^{\text{loc}}(E) - t_{nL\downarrow\downarrow}^{\text{loc}}(E)) \sigma_z \right] U_n^\dagger
$$

(11)

with $\sigma_z$ is the $z$ component of the Pauli matrices:

$$
\sigma_z = \begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
$$

(12)

It is convenient to define the projection matrices $\sigma_{ns}$ for the local spin–up ($\uparrow$) and spin–down ($\downarrow$) directions as:
\[
\sigma_{ns} = \frac{1}{2} U_n (1 \pm \sigma_z) U_n^\dagger = (\sigma_{ns})^2 \quad (+ \text{ for } s = \uparrow, - \text{ for } s = \downarrow)
\]

Then \(t_n^{\text{glob}}(E)\) is written as:

\[t_n^{\text{glob}}(E) = t_{n\uparrow\uparrow}^{\text{loc}}(E)\sigma_{n\uparrow} + t_{n\downarrow\downarrow}^{\text{loc}}(E)\sigma_{n\downarrow}\]  \(\text{(collinear case).} \quad (14)\)

In the collinear case the local and global frames are identical and the projection operators reduce to:

\[
\sigma_{\uparrow} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad \sigma_{\downarrow} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \quad \text{(collinear case).} \quad (15)
\]

At this stage, the difference between the \(t\)-matrices \(\Delta t_n^{\text{glob}} = t_n^{\text{glob}} - t_n\) is calculated in order to get all the ingredients to solve the Dyson equation for the structural Green function (\(\hat{t}_n\) has been defined in the global frame in Eq. (8)). This is the analogue of Eq. (2) in matrix form in spin space:

\[G_{\text{str}}(E) = G_{\text{str}}(E) + G_{\text{str}}(E) \Delta t_n^{\text{glob}}(E) G_{\text{str}}(E). \quad (16)\]

Here, in analogy to eq. (11) and eq. (2), \(G_{\text{str}}(E)\) are matrices of size \(2 \times 2\) in spin space, size \((l_{\text{max}}+1)^2 \times (l_{\text{max}}+1)^2\) in angular momentum space, and size \(N \times N\) (with \(N\) the number of sites) in real space; all these indices are combined to form \(2 \times (l_{\text{max}}+1)^2 \times N\)-dimensional matrices. The \(t\)-matrix itself is diagonal in real space site indexes. The solution of Eq. (16) for the structural Green function requires matrix inversion, yielding \(G_{\text{str}}(E)\) in the global frame:

\[G_{\text{str}}(E) = G_{\text{str}}(E)(1 - \Delta t_n^{\text{glob}}(E) G_{\text{str}}(E))^{-1}. \quad (17)\]

Equation (11) can be now rewritten in the non-collinear case in order to obtain the Green function in the global frame. Using the matrices \(\sigma_{ns}\) (Eq. (13)) to project the local wavefunctions to the global frame, the Green function is written as:

\[
G_{\text{str}}(E) = G_{\text{str}}(E) + G_{\text{str}}(E) \Delta t_n^{\text{glob}}(E) G_{\text{str}}(E) \quad \text{(non-collinear).} \quad (18)
\]

If needed, the Green function can be rotated to the local frame of any atom by the use of the transformation matrices \(U_n\) (Eq. (11)). We point out that, even in the local frame of reference, the Green function is not in general diagonal in spin space. Finally we calculate the charge density and spin density from Equations (3,4). The spin diagonal in spin space. Finally we calculate the charge density and spin density from Equations (3,4). The spin density \(\rho_{n\sigma}(\vec{r})\) (Eq. (11)) is non-collinear. The new polar angles at each site \(n\) can then be obtained for each point by

\[
\tan \theta_n(\vec{r}) = \frac{m_{\uparrow}(\vec{r})}{m_{\downarrow}(\vec{r})}, \quad \tan \phi_n(\vec{r}) = \frac{m_{\uparrow}(\vec{r})}{m_{\downarrow}(\vec{r})} \quad \text{(collinear).} \quad (20)
\]

or as an average over the local Wigner–Seitz cell

\[
\tan \theta_n = \frac{\int_{\text{WS}} m_{\uparrow}(\vec{r}) d\vec{r}}{\int_{\text{WS}} m_{\downarrow}(\vec{r}) d\vec{r}}, \quad \tan \phi_n = \frac{\int_{\text{WS}} m_{\uparrow}(\vec{r}) d\vec{r}}{\int_{\text{WS}} m_{\downarrow}(\vec{r}) d\vec{r}} \quad \text{(non-collinear).} \quad (21)
\]

III. APPLICATIONS

As an application of our method, we study the magnetic state of 3d-atom clusters in and on the Ni(001) surface. In a first step, we study the adatom properties, which are already known from previous work. In a second step, we perform calculations for 3d dimers and trimers and use the understanding gained from the single adatoms in order to explain the results.

Our calculations henceforth are based on the Local Spin Density Approximation (LSDA) of density functional theory with the parametrization of Vosko et al.\(^{32}\). The full non-spherical potential was used, taking into account the correct description of the Wigner–Seitz atomic cells.\(^{33}\) Angular momenta up to \(l_{\text{max}} = 3\) were included in the expansion of the Green functions and up to \(2l_{\text{max}} = 6\) in the charge density expansion. Relativistic effects were described in the scalar relativistic approximation.

First, the surface Green functions are determined by the screened KKR method\(^{33}\) for the (001) surface of Ni which serves as the reference system. The equilibrium lattice parameter of Ni was used (6.46 a.u. \(\approx 3.42\) Å). To describe the impurities on the surface (later we refer to these as adatoms) and to the impurities sitting in
the first surface layer as inatoms), we consider a cluster of perturbed potentials which includes the potentials of the impurities and the perturbed potentials of several neighboring shells, with typical size ranging from 19 perturbed sites for the single impurity to 32 for the dimers and trimers; in all cases, at least the first neighboring sites of the impurity atoms were taken into account in the calculation to ensure the correct screening of the impurity potential. Test calculations have shown that this is adequate for our work; this is a merit of the Green function method, in which the correct boundary conditions of the host (in our case of the host surface) are included in the Green function via the Dyson equation. We consider the adatoms at the unrelaxed hollow position in the first vacuum layer, and the inatoms at the unrelaxed position in the first surface layer.

The orientations assigned to the spin moments of the impurities are always relative to the orientation of the substrate moment, which we take as the global frame. This, in turn, depends on delicate physical quantities such as the magnetic anisotropy energy, which cannot be related to the local properties of the small clusters that we study. In the present approach such effects arising from spin–orbit interaction are not included. The direction of the host moments must therefore be considered as an input parameter from experiments or from independent ab-initio calculations.

A. 3d single adatoms and inatoms

3d adatoms on Fe(001) and on Ni(001) have been already studied previously, using the KKR method in the atomic sphere approximation. Here we repeat the calculations of 3d adatoms on Ni(001) using the full potential method (a detailed work on Fe and Co on Ni(001) is presented in a recent article). We give a brief analysis of the results, which are basically unchanged, in order to use them as a step for understanding the behavior of dimers and trimers later on.

A collinear calculation of the magnetic state of a single adatom on a ferromagnetic substrate can give in some cases two solutions: one with ferromagnetic coupling (FM) to the substrate and one with antiferromagnetic coupling (AF). One of these states will correspond to the real ground state, and the other to a local minimum; this is actually a local minimum with respect to collinear variations of the magnetic moment, since the angle $\theta$ between the local moment and the substrate moment cannot be varied in a collinear calculation. From total energy calculations of the two states, the ground state can be then determined. In some cases, when the intra-atomic exchange field is not strong (beginning or end of the 3d series), only one of the two minima exists. On the other hand, if non-collinear effects are included in the calculations, one of the two minima usually becomes unstable against an angular rotation of the moment, i.e., it is then actually a saddle point.

The full diamonds in the Fig. (a) show the energy difference between the AF and FM coupling, the values related to adatom and inatom are described by respectively full and empty black diamonds; (b) magnetic moments of the adatoms (black triangles) and inatoms (green circles) within the 2 possible magnetic configurations FM and AF; (c) the variation of the magnetic moments of Ni first Nearest Neighbors of the adatoms.

![Graph showing energy difference and magnetic moments](image-url)

FIG. 1: 3d adatoms and inatoms on Ni(001): (a) Energy difference between the AF and FM coupling, the values related to adatom and inatom are described by respectively full and empty black diamonds; (b) magnetic moments of the adatoms (black triangles) and inatoms (green circles) within the 2 possible magnetic configurations FM and AF; (c) the variation of the magnetic moments of Ni first Nearest Neighbors of the adatoms.
on the contrary, the minority $d$ VBS is at $E_F$, and this aligns with the Ni minority $d$ states; then a FM coupling arises. For our purposes we keep in mind that, since Cr and Mn are in the intermediate region, i.e., near the AF-FM transition point, their magnetic coupling to the Ni substrate is weak; this has consequences to be seen in the behavior of dimers, trimers, etc., in the next subsections.

The magnetic moments of the adatoms and Ni first neighbors in the surface layer are shown in Fig. 1b) and (c). Evidently the moment of the Ni first neighbors is strongly affected by the adatoms. Especially in the AF state for Mn, Fe, and Co adatoms, the Ni moment is strongly reduced and the FM configuration is stable. As regards the adatom moments, due to its half filled d band the Mn adatom carries the highest magnetic moment (4.09 $\mu_B$) followed by Cr (3.48 $\mu_B$) and Fe (3.24 $\mu_B$).

To understand the effect of coordination and stronger hybridization on the magnetic behavior of the adatoms, we take the case of impurities sitting in the first surface layer (inatoms). We carried out the calculations for V, Cr, Mn, Fe and Co impurities. The corresponding spin moments are shown in Fig. 1b (green circles), and the FM-AF energy differences are shown in Fig. 1a (open diamonds and dashed line).

Compared to the adatom case, the spin moments are reduced, especially for V and Cr. This effect is expected due to the increase of the coordination number from 4 to 8 and the subsequent stronger hybridization of the 3$d$ levels with the host wavefunctions. Moreover, the energy difference $\Delta E$ between the AF and FM solutions is affected. The trend can be understood as follows. In the case of Cr, the reduction of the local magnetic moment $M$ is accompanied by a reduction of the exchange splitting $\Delta E_X$ as $\Delta E_X \approx I \cdot M$, where $I \approx 1$ eV is the intra-atomic exchange integral. This means that, for the inatom, the occupied 3$d$ states are closer to $E_F$ than for the adatom. In turn, this intensifies the hybridization of these states with the Ni 3$d$ states (which are close to $E_F$). At the same time, also the higher coordination number intensifies the $d$-$d$ hybridization. The hybridization-induced level shift in the AF configuration increases, and the energy of the AF state is thus lowered. The same mechanism is responsible for the weakening of the FM coupling of Mn in-atoms compared to the adatom. Similarly, the stronger hybridization of the Co-inatom $d$-states stabilizes even more its FM configuration due to the energy gain from the broadening of the $d$ virtual bound state.

**B. Adatom and inatom dimers**

Having established the single adatom behavior, we turn to adatom dimers. We considered three geometries of increasing distance: dimers as first, second, and fourth neighbors. We will discuss the magnetic interaction between the dimer atoms and the resulting magnetic order, first looking only at collinear states and then allowing for non-collinear order. We will see how, in certain cases, the collinear state reduces the symmetry, while the non-collinear state restores the full symmetry of the system. Non-collinear order is finally established for certain first-neighbor dimers.

Fig. 3 represents schematically the different considered geometrical configurations of impurity dimers residing on the surface. We have investigated the dimer-1-type of geometry (the adatoms are first neighboring atoms), dimer-2-type (the adatoms are second neighbors) and dimer-3-type (the adatoms are fourth neighbors). This allows us to monitor the strength of the magnetic coupling as a function of the distance. Three collinear magnetic configurations were treated: (i) antiferromagnetic coupling within the dimer leading to a ferrimagnetic solution (Ferri), (ii) ferromagnetic coupling within the dimer with both atoms ferromagnetically coupled to the substrate (FM), or (iii) ferromagnetic coupling within the dimer with both atoms antiferromagnetically coupled to the substrate (AF).

Our calculations include V, Cr, Mn and Fe dimers. We found that all V and Fe dimer types behave like the adatoms: in all geometries, both V atoms are AF and both Fe atoms are FM. On the other hand, Cr and Mn dimers show magnetic frustration. As shown in Fig. 3, both the Cr–dimer-1 and Mn–dimer-1 show (in a collinear calculation) a Ferri ground state (see Table 1). With increasing distance between the adatoms, a transition occurs to the single adatom magnetic behavior which is AF for Cr–dimers and FM for Mn–dimers. It is clear that, in the dimer-1 case, there is a competition of exchange interactions.

When we allow for a rotation of the magnetic moments, non-collinear solutions are obtained for the Cr– and Mn–dimer-1 systems. On the other hand the magnetic coupling of the V– and Fe–dimer-1 remains collinear. Let us start with Cr–dimer-1: Fig. 4a) represents the collinear magnetic ground state. As one expects from the adatom picture, both adatoms forming the dimer tend to couple AF to the substrate but due to their half filled $d$ band they also tend to couple AF to each other. This can be understood in terms of the Alexander–Anderson model. To give a short explanation (see Fig. 2), both Cr and Mn have their majority–spin VBS occupied, below $E_F$, and the minority–spin VBS unoccupied, above $E_F$. An antiparallel configuration between the moments in a Mn or Cr dimer lowers the energy, because the occupied $d$ VBS of each atom hybridizes with the unoccupied $d$ VBS of the other atom and is shifted to lower eigenvalues. Contrary to this, a parallel coupling does not lower the energy, since there is no level shifting, but only level broadening of the majority $d$–VBS. Since these are fully occupied, the broadening brings no energy gain.

Thus there is a competition between the interatomic coupling within the dimer, which drives it to a Ferri state, and the exchange interaction with the substrate, which drives the moments of both atoms in the same direction: AF for Cr and FM for Mn. As discussed in the
previous subsection, the magnetic exchange interaction (MEI) to the substrate is relatively weak for Cr and Mn. Thus, the intra-dimer MEI is stronger than the MEI with the substrate, and in the collinear approximation the ground state is found ferrimagnetic (Ferri). Removing the collinear constraint, a compromise can be found such that both atoms are AF coupled to each other and at the same time (for Cr) slightly AF coupled to the substrate. This is shown in Fig. 5(b): the Cr adatom moments are aligned antiparallel to each other and basically perpendicular to the substrate moments. However, the weak AF interaction with the substrate causes a slight tilting towards the substrate, leading to an angle of 94.2° instead of 90°. We also observe a very small tilting ($\approx 0.3°$) of the magnetic moments of the four outer Ni atoms neighboring the Cr dimer (the two inner Ni atoms do not tilt for symmetry reasons).

Despite the above considerations, the collinear Ferri state (Fig. 4(a)) is also a self-consistent solution of the Kohn-Sham equations, even if the collinear constraint is removed. Total energy calculations are needed in order to determine if the non-collinear state is the true ground state, or if it represents a local minimum of energy with the collinear result representing the true ground state. After performing such calculations we find that the ground state is collinear with an energy difference of $\Delta E_{\text{Ncol-Ferri}} = 39.84$ meV (increasing the angular-momentum cutoff to $l_{\text{max}} = 4$ brought no significant change to this result).

The case is different for Mn dimers. Fig. 5 shows the collinear and the non-collinear solutions. The dimer atoms couple strongly antiferromagnetically to each other but the single Mn adatoms tend to couple (weakly) ferromagnetically to the substrate. Both adatom moments, while aligned AF with respect to each other, are tilted in the direction of the substrate magnetization, as opposed to the Cr–dimer. With a rotation angle of $\approx 72.6°$, the tilting from the 90° configuration is rather large. Also the Ni moments are tilted by $7.4°$. The main difference with the case of Cr–dimer-1 is that for Mn–dimer-1 the non-collinear solution is the ground state (total energy calculations yield $\Delta E_{\text{Ncol-Ferri}} = -13.45$ meV). The spin moments of the V, Cr, Mn, and Fe dimers are given in Table III.

In both cases (Cr and Mn dimers) the frustrated collinear solution is asymmetric, while the non-collinear ground state restores the twofold symmetry of the system. The differences in energy between the Ferri and the non-collinear solutions are small and can be altered either by using a different type of exchange and correlation functional such as GGA or LSDA+$U$, or after relaxing the atoms. We note, however, that in a test calculation

\begin{center}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
 & Cr & & & Mn & & \\
 & Dimer 1 & Dimer 2 & Dimer 3 & Dimer 1 & Dimer 2 & Dimer 3 \\
\hline
$E_{\text{FM}} - E_{\text{Ferri}}$(eV) & 0.451 & 0.130 & 0.120 & 0.065 & -0.242 & -0.239 \\
$E_{\text{AF}} - E_{\text{Ferri}}$(eV) & 0.433 & -0.093 & -0.112 & 0.496 & 0.187 & 0.233 \\
\hline
\end{tabular}
\end{center}

TABLE I: Energy differences between the Ferri solution and the FM (AF) configuration for the three types of dimers investigated.
we found the Cr single-adatom relaxation to be small (3.23 % inward with respect to the interlayer distance), and thus we believe that the relaxation cannot affect the exchange interaction considerably.

As a cross-check, it is interesting to compare these non-collinear \textit{ab-initio} results to model calculations based on the Heisenberg model with the exchange parameters fitted to the total energy results. We assume a classical spin Hamiltonian of the form

\[ H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \vec{e}_i \cdot \vec{e}_j. \]  

(22)

Here, $\vec{e}$ is a unit vector defining the direction of the magnetic moment and $i$ and $j$ indicate the dimer atoms and their first Ni neighbors. We can evaluate the interatomic exchange constants $J_{\text{Cr--Ni}}$, $J_{\text{Mn--Ni}}$, $J_{\text{Mn--Mn}}$, and $J_{\text{Cr--Cr}}$ via a fit to the total energy obtained from collinear LSDA calculations of the FM, AF, and Ferri configurations. Taking into account only first-neighbor interactions and neglecting the rotation of Ni moments, we rewrite the Hamiltonian for the dimer in terms of the tilting angles $\theta_1$ and $\theta_2$ of the two Cr (or Mn) atoms (the azimuthal angles $\phi$ do not enter the expression because of symmetry reasons):

\[ H = -J_{\text{Cr--Cr}} \cos(\theta_1 - \theta_2) - 4J_{\text{Cr--Ni}}(\cos \theta_1 + \cos \theta_2) + \text{const}. \]  

(23)

We note the two extreme cases arising from this Heisenberg Hamiltonian: (i) $|J_{\text{Cr--Ni}}| \gg |J_{\text{Cr--Cr}}|$ leads to the stabilization of the collinear FM or AF configuration (adatom-like behavior) and (ii) $|J_{\text{Cr--Ni}}| \ll |J_{\text{Cr--Cr}}|$ leads to antiferromagnetic coupling within the dimer if $J_{\text{Cr--Cr}} < 0$. Within the Heisenberg model the Ferri solution and the non-collinear solution with $\theta = 90^\circ$ have the same energy.

Table II summarizes the estimated exchange parameters. Two effects are striking: (i) The strong antiferromagnetic Cr–Cr and Mn–Mn interaction for the dimer-1 (nearest neighbors), being an order of magnitude larger than the exchange interactions with the substrate and being responsible for the stabilization of the non-collinear state structures shown in Figs. 4 and 5. (ii) The very weak Cr–Cr and Mn–Mn interactions in the dimer-2 and -3 configurations. Whereas for the nearest-neighbors configuration (dimer-1) the direct overlap of the $d$–wavefunctions of the Cr and Mn atoms leads to the strong coupling, this overlap is missing for larger distances and the interaction can only proceed through the substrate. However, this interaction is weak, in fact considerably smaller than the interaction of both adatoms with the four neighboring Ni atoms of the substrate. Therefore these dimers are effectively decoupled, and behave like the isolated adatoms, being antiferromagneti-
TABLE II: Values of magnetic exchange parameters $J_{ij}$ for Cr and Mn dimers on Ni(001), fitted from collinear first-principles total energy calculations (b) and obtained by the Lichtenstein formula (a) ($J_{Cr-Ni}$ and $J_{Mn-Ni}$ are averaged over the different Ni first neighbours of the dimer atoms). Positive $J_{ij}$ correspond to ferromagnetic interactions, negative $J_{ij}$ to antiferromagnetic ones.

|          | (a)       |          | (b)       |          |
|----------|-----------|----------|-----------|----------|
| $J_{ij}$ (meV) | Dimer 1 | Dimer 1 | Dimer 2 | Dimer 3 |
| $J_{Cr-Ni}$   | -1.3     | -11.6    | -13.9    | -14.5    |
| $J_{Cr-Cr}$   | -189.1   | -221.3   | -9.2     | -2.0     |
| $J_{Mn-Ni}$   | 13.0     | 27.0     | 26.8     | 29.5     |
| $J_{Mn-Mn}$   | -138.2   | -140.2   | 13.7     | 1.5      |

With the parameters from Table III one can also recalculate the non-collinear structure of the ground state. The agreement with the ab-initio results is quite reasonable. For the Cr dimer, one finds a slightly smaller tilting, i.e. 96° instead of 94.2°, while for the Mn dimer the angle is 67.3° instead of 70.6°.

The differences in energy calculated within this simple model, show that the Cr-dimer-1 has a non-collinear ground state ($\Delta E_{\text{Ncol–Ferri}} = -9.7$ meV) as well as the Mn-dimer-1 ($\Delta E_{\text{Ncol–Ferri}} = -41.6$ meV). The discrepancy obtained for the case of Cr-dimer-1 (the LSDA calculation gives the collinear Ferri ground state) can be attributed to the restrictions of the Heisenberg model. For instance, for the Cr and non-collinear configurations, the Cr moments are slightly different, and also the reduction of the Ni moments as a function of the rotation angle (e.g. for the single adatom) cannot be described by the Heisenberg model, where the absolute values of the moments are assumed to be constant. Within the Heisenberg model, the Ferri solution (with $\theta_1 = 0°$ and $\theta_2 = 180°$) is degenerate with the non-collinear solution ($\theta_{1,2} = 90°$ with AF coupling within the dimer).

To evaluate the effect of change in coordination and hybridization, we have undertaken a study of inatom first-neighbor dimers for V, Cr, Mn and Fe. The V and Fe inatom-dimers were found to behave like the adatom dimers. The V dimer is in an AF state, the Fe dimer in a FM state, while the Cr and Mn dimers are in a Ferri state (in case of collinear constraint). The spin moments in the collinear and non-collinear states are given in Table III. Within the Ferri-dimers, the difference between the moments of the two atoms is due to the different kind of coupling that each inatom has with the substrate (AF or FM). One notices also that the magnetic moments in the ground state decrease compared to the values obtained for the single inatoms and single adatoms. When the rotation of the moments is allowed, Cr–dimer can be stabilized at an angle of 107° (instead of 94.2° found for the adatom–dimer case), and Mn–dimer at an angle of 80.9° (instead of 72.6°). Thus the non-collinear solutions obtained for inatom–dimers are rather similar to what was obtained for adatom–dimers. Energetically, however, both the Cr and the Mn inatom dimers show a lower total energy in the collinear Ferri state (for Cr, $\Delta E_{\text{Ncol–Ferri}} = 24.11$ meV; for Mn, $\Delta E_{\text{Ncol–Ferri}} = 22.5$ meV).

C. Trimers

Following the same procedure as for dimers we first investigated several collinear magnetic configurations for the most compact trimer on the Ni(001) surface, which has the shape of an isosceles rectangular triangle (see Fig. R of side $\sqrt{2}a/2$ and hypotenuse $a$ (a is the Ni fcc lattice constant). It is expected, and verified by total-energy calculations, to find the $\uparrow\downarrow\downarrow$ configuration as the collinear magnetic ground state for Cr and the $\uparrow\uparrow\uparrow$ for the Mn trimer ($\uparrow$ means an atomic moment parallel to the substrate, $\downarrow$ an antiparallel one; the middle arrow represents the direction of the atomic moment at the right-angle corner of the triangle). In Table IV the energy differences among the possible collinear configurations are given: for the $\uparrow\uparrow\uparrow$ and $\downarrow\downarrow\downarrow$ Cr trimers, no self-consistent solution could be found.

Allowing free rotation of the magnetic moments leads to no change for the Cr trimer $\uparrow\downarrow\downarrow$—the state remains collinear (within numerical accuracy). On the other hand, for the Mn trimer a non-collinear solution is found (Fig. R with the nearest neighbours almost antiferromagnetic to each other, but with a collective tilting angle with respect to the substrate. This tilting angle is induced by the ferromagnetic MEI between the central Mn atom with the substrate, competing with the antiferromagnetic MEI with its two companions. The top view...
The surface atoms experience small tilting, with varying angles around 4°–10°. From the energy point of view, the ground state is the collinear one, \( \uparrow\downarrow\uparrow \), with an energy difference of \( \Delta E_{\text{Ncol}}=22.92 \) meV with respect to the non-collinear solution.

We have also investigated the cases where the trimers are sitting in the surface layer. No non-collinear solution was found, while there is no change in the collinear ground state which is \( \downarrow\uparrow\downarrow \) for the Cr trimer and \( \uparrow\uparrow\uparrow \) for Mn trimer.

One should note that the moments of the two first neighboring impurities are almost compensated in the Ferri solution. The third moment determines the total interaction between the substrate and the trimer which has then a net moment coming mainly from the additional impurity. This interaction is identical to the single adatom (or inatom) type of coupling.

### IV. SUMMARY

We have presented a formalism for the treatment of non-collinear magnetic clusters on surfaces and in bulk, based on the Green function technique of Korringa, Kohn and Rostoker, and on spin density functional theory. We have applied the formalism on the study of small transition metal clusters (dimers and trimers) on and in the Ni(001) surface.

Emphasis was placed on Cr and Mn clusters, for which we found that magnetic frustration can lead to non-collinear magnetic order. The origin of the frustration is the competition of the antiferromagnetic exchange coupling among the Cr or Mn atoms with the antiferromagnetic (for Cr) or ferromagnetic (for Mn) exchange coupling between the adatoms and the substrate. In this respect, the result is different than the prototype non-collinear configurations arising from antiferromagnetic interactions among atoms in triangular geometry.

We found that Cr and Mn first-neighbouring adatom dimers can show non-collinear behavior, while increasing the distance between the adatoms of the dimer leads to the same state as for single adatoms. The energy differences between the collinear ferrimagnetic state and the non-collinear one are \( \Delta E_{\text{Ncol}}^{\text{Cr}}=39.84 \) meV (the ground state is collinear), \( \Delta E_{\text{Ncol}}^{\text{Mn}}=-13.45 \) meV (the ground state is non-collinear). Embedding the dimers in the first surface layer restores the Ferri collinear solution as a ground state also for Mn adatom dimers (\( \Delta E_{\text{Ncol}}^{\text{Mn}}=24.11 \) meV, \( \Delta E_{\text{Ncol}}^{\text{Mn}}=-22.5 \) meV).

Our \textit{ab-initio} results for dimers are compared to the solution of a classical Heisenberg model with exchange parameters fitted to total energy calculations. The agreement for the tilting angles in the non-collinear state is good, but the Heisenberg model does not capture the collinear ground state for the Cr dimer. This discrepancy occurs because the Heisenberg model is restricted to constant absolute values of localized spins.

The trimers studied so far are characterized by a collinear ground state: \( \uparrow\downarrow\uparrow \) for the Cr trimer and \( \uparrow\uparrow\uparrow \) for the Mn trimer. The Cr trimer has also a non-collinear metastable solution with an energy difference \( \Delta E_{\text{Ncol}}=24.11 \) meV, \( \Delta E_{\text{Ncol}}^{\text{Mn}}=-22.5 \) meV.

We believe that the energetic proximity of the collinear to the non-collinear states is directly related to the weakness of the exchange interaction with the Ni substrate. Replacing it by an fcc Fe substrate will possibly change the ground state drastically. Work in this direction progress and will be reported elsewhere.

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| Dimer type | V(AF) | Cr(Ferri) | Cr(Ncol) | Mn(Ferri) | Mn(Ncol) | Fe(FM) |
|------------|-------|-----------|----------|-----------|----------|--------|
| On Ni(001) | (-1.28, -1.28) | (-3.04, 3.05) | (3.03, 3.03) | (-3.84, 3.69) | (3.75, 3.75) | (3.10, 3.10) |
| In Ni(001)  | (-0.32, -0.32) | (-2.00, 1.96) | (1.97, 1.97) | (-3.32, 3.20) | (3.26, 3.26) | (2.88, 2.88) |

**TABLE III:** Atomic spin moments (in \( \mu_B \)) of the adatom and inatom dimers (of type 1, i.e., nearest-neighbors) in the collinear and non-collinear configurations. A minus sign of the collinear moments indicates an antiparallel orientation with respect to the substrate magnetization. Embedding the dimer into the surface causes, as expected, a decrease of the spin moments due to stronger hybridization of the d wavefunctions.

| Magn. Config. | \( \uparrow\downarrow \) | \( \downarrow\uparrow\uparrow \) | \( \uparrow\uparrow\uparrow \) | \( \uparrow\downarrow\uparrow \) |
|---------------|----------------|----------------|----------------|----------------|
| Cr: \( E - E_{\text{Ncol}}^{\text{Cr}} \) (eV) | 0.420 | 0.390 | 0.193 | — |
| Mn: \( E - E_{\text{Ncol}}^{\text{Mn}} \) (eV) | 0.116 | 0.318 | -0.184 | 0.239 | 0.817 |

**TABLE IV:** Energy differences between the different calculated collinear magnetic configurations with the \( \downarrow\uparrow\uparrow \) configuration. The direction of the arrows represents the direction of the atomic moments relative to the substrate magnetization (\( \uparrow \) parallel, \( \downarrow \) antiparallel). The middle arrow represents the atom at the right-angle corner of the trimer.
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