

***Ab Initio* approach for atomic relaxation in supported magnetic clusters**

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We present a newly developed scheme for atomic relaxations of magnetic supported clusters. Our approach is based on the full potential Korringa–Kohn–Rostoker Green’s function method and the second moment tight-binding approximation for many-body potentials. We demonstrate that only a few iterations in *ab initio* calculations are necessary to find an equilibrium structure for supported clusters. As an example, we present our results for small Co clusters on Cu(001). Changes in the electronic and magnetic states of the clusters due to atomic relaxations are revealed.

Keywords: *Ab initio* calculations; Tight-binding approximation; Atomic relaxations

1. Introduction

One of the central issues in the physics of nanostructures is the interplay between atomic structure, and electronic and magnetic states. Different empirical and semi-empirical potentials have been used to determine the interatomic interactions [1]. These analytic potential energy functions can be considered as simplified mathematical expressions for modeling interatomic forces arising from quantum mechanical interactions. Parameters of such potentials are usually fitted to bulk properties, which include lattice constants, cohesive energies, bulk modulus, elastic properties and vacancy formation energies. Although these methods have given important results for cluster formation, their interactions and diffusion on metal surfaces, they become less effective for a quantitative description of structural relaxations in transition metal clusters on surfaces. The lack of a detailed description of electronic states is also an obvious drawback of analytical potential energy functions. Calculations of structural relaxations, and electronic and magnetic properties of small magnetic clusters on metal surfaces have recently been performed using quantum-chemical methods [4]. The metal surface in such calculations

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is approximated by a finite atomic cluster. One of the difficulties associated with the use of a cluster to model an infinite or semi-infinite system is that the cluster size is usually small due to computational limitations, and one must be sure that this limitation does not lead to spurious conclusions.

Recently, we developed N -body interatomic potentials formulated in the second moment tight-binding approximation (TB-SMA) [2]. Parameters of potentials are fitted to accurate first-principle calculations of selected cluster–substrate properties. This scheme allows us to correctly reproduce the bonding in transition metal clusters on metal surfaces. Several applications of our potentials can be found in recent publications [2, 3, 7, 8, 10]. In this work we show that *ab initio*-fitted many-body potentials and the KKR Green’s function method can be combined to perform fully *ab initio* relaxations of magnetic clusters on semi-infinite metal substrates. Many-body potentials are used to approximate the trajectories of atoms during relaxation. *Ab initio* Hellmann–Feynman (HF) forces are calculated to find an equilibrium structure. The structure and electronic and magnetic states are calculated self-consistently. We concentrate on small Co clusters on Cu(100).

2. Method

First, we describe the KKR Green’s function method used for calculations of forces acting on atoms in supported clusters, and their electronic and magnetic properties [5, 11]. The basic idea of the method is a hierarchical scheme for the construction of the Green’s function of clusters on a metal surface by means of successive applications of Dyson’s equation. We treat the surface as a two-dimensional perturbation of the bulk. For the calculation of the ideal surface the nuclear charges of several monolayers are removed, thus creating two half-crystals that are practically uncoupled. Taking into account the 2D periodicity of the ideal surface, we find the structural Green’s function by solving a Dyson equation self-consistently:

$$G_{LL'}^{jj'}(\mathbf{k}_{\parallel}, E) = \overset{\circ}{G}_{LL'}^{jj'}(\mathbf{k}_{\parallel}, E) + \sum_{j''L''} \overset{\circ}{G}_{LL''}^{jj''}(\mathbf{k}_{\parallel}, E) \Delta t_{L''}^{j''}(E) G_{L''L'}^{j''j'}(\mathbf{k}_{\parallel}, E). \quad (1)$$

Here, $\overset{\circ}{G}$ is the structural Green’s function of the bulk in a \mathbf{k}_{\parallel} layer representation (j, j' , layer indices). The \mathbf{k}_{\parallel} wave vector belongs to the 2D Brillouin zone. $\Delta t_L^j(E)$ is the perturbation of the t matrix to angular momentum $L = (l, m)$ in the j th layer.

The consideration of clusters on the surface destroys the translation symmetry. Therefore, the Green’s function of the cluster on the surface is calculated in a real space formulation. The structural Green’s function of the ideal surface in real space representation is then used as the reference Green’s function for the calculation of the cluster–surface system from an algebraic Dyson equation:

$$G_{LL'}^{nm'}(E) = \overset{\circ}{G}_{LL'}^{nm'}(E) + \sum_{n''L''} \overset{\circ}{G}_{LL''}^{nm''}(E) \Delta t_{L''}^{n''}(E) G_{L''L'}^{n''n'}(E), \quad (2)$$

where $G_{LL'}^{nm'}(E)$ is the energy-dependent structural Green’s function matrix and $\overset{\circ}{G}_{LL''}^{nm''}(E)$ is the corresponding matrix for the ideal surface, serving as a reference system. $\Delta t_L^n(E)$ describes the difference in the scattering properties at site n induced by the existence of the adsorbate atom. Exchange and correlation effects are included in the local density approximation. The full charge density and the

full potential are used in our calculations. For atomic relaxations of clusters we transform the Green's function of the cluster into the shifted coordinate system using the transformation matrix [5]. In solving Schrödinger and Poisson equations we use the shape function. For distorted atomic positions we make a Wigner–Seitz (WS) construction in the distorted geometry. We apply the ionic Hellmann–Feynman formula for calculations of forces acting on atoms [5].

Many-body potentials are formulated in the second moment tight binding approximation [2]. The attractive term (band energy) E_B^i contains the many-body interaction. The repulsive term E_R^i is described by pair interactions (Born–Mayer form). The cohesive energy E_{coh} is the sum of the band energy and repulsive part:

$$E_{\text{coh}} = \sum_i (E_R^i + E_B^i), \quad (3)$$

$$E_R^i = \sum_j A_{\alpha\beta} \exp\left(-p_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1\right)\right), \quad (4)$$

$$E_B^i = -\left(\sum_j \xi_{\alpha\beta}^2 \exp\left(-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1\right)\right)\right)^{1/2}, \quad (5)$$

where r_{ij} is the distance between atoms i and j , $r_0^{\alpha\beta}$ is the first-neighbour distance in the crystalline structure of the pure metals for atom-like interactions and becomes an adjustable parameter in the case of the cross-interaction, ξ is an effective hopping integral, and $p_{\alpha\beta}$ and $q_{\alpha\beta}$ describe the decay of the interaction strength with distance between the atoms.

Binding energies of supported and embedded clusters of different sizes and geometry, the HF forces acting on adatoms and the surface energies are accurately fitted to the *ab initio* results to find the parameters of the potentials. It should be noted that the bonds of low-coordinated atoms are considerably stronger than bonds in the bulk. Therefore, surface properties should be included in the fitting of potentials to correctly describe atomic relaxations in supported clusters. To link the interaction between atoms on the surface to that in the bulk the set of data used for fitting also includes bulk properties such as the bulk modulus, lattice constant, cohesive energy, and elastic constants. The combination of *ab initio* and TB methods allows one to construct many-body potentials for low-dimensional structures and to perform atomic relaxations for very large systems. Parameters of potentials for Fe, Co and Cu nanostructures on Cu substrates can be found in our recent publications [2, 3, 9]. Here, we show that these potentials can be used to perform fully *ab initio* atomic relaxations by means of the KKR Green's function method. The key idea of our approach is presented in figure 1. First, we find the relaxed atomic configuration of the cluster on the surface using *ab initio*-fitted many-body potentials. We call these potentials the trial potentials. This structure is used to perform the *ab initio* self-consistent calculations by means of the KKR Green's function method. Then, we calculate the HF forces acting on each atom. If these forces are not equal to zero, the potentials are fitted again to correctly reproduce these *ab initio* forces. The structure of the cluster is again relaxed with new fitted potentials. We repeat the calculations until the *ab initio* forces are very small, i.e. the cluster is fully relaxed. It should be noted that, in fact, *ab initio* relaxations of supported clusters without the use of potentials are possible, however they require

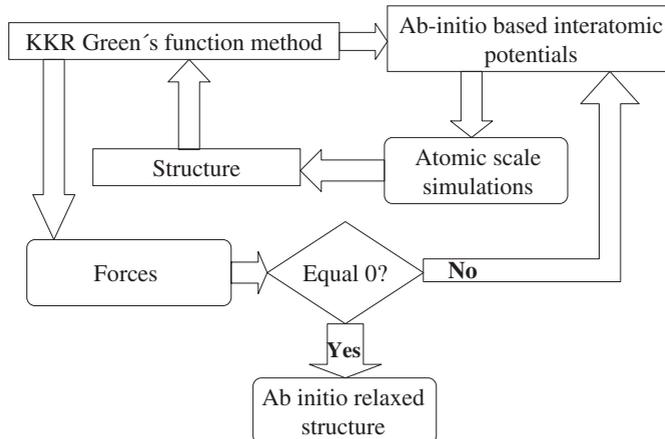


Figure 1. Schematic representation of the method for relaxation of supported clusters. KKR Green's function method and *ab initio*-fitted many-body potentials are used to determine the structure and the electronic and magnetic states in clusters fully self-consistently.

much more computational effort. The problem is that any small change in the position of an atom of the cluster during relaxation leads to large changes in the forces acting on different atoms. *Ab initio*-fitted many-body potentials allow us to find a very good approximation for the displacements of the atoms at each iteration. In other words, potentials 'help' the *ab initio* method to find the correct atomic displacements. We will show that only six to seven iterations should be performed to fully relax small magnetic clusters. The magnetic and electronic properties of clusters are determined self-consistently at each iteration.

3. Small Co clusters on Cu(001)

First, we discuss in detail the results for the Co_4 cluster. As the first application of the method, we present calculations for atomic relaxations in clusters on an ideal Cu substrate. *Ab initio* relaxations of the substrate atoms can also be performed using our approach. However, as we will see in this section, *ab initio*-based potentials give a very good approximation to the fully *ab initio* results. Therefore, we believe that reliable results for atomic relaxations in the substrate can simply be obtained using our potentials without performing fully *ab initio* calculations [3, 8, 10]

In figure 2 we present the potentials for Co–Cu and Co–Co interactions obtained by fitting to *ab initio* results (the trial potentials). Using these potentials we carried out relaxation of the structure of the Co_4 cluster. The bond length and the vertical coordinates of atoms before and after relaxation are summarized in Table 1. One can see that the relaxed bond length and the relaxed distance to the substrate vary from the unrelaxed values by as much as 0.2 \AA and 0.07 \AA , respectively. For the relaxed structure of the Co_4 cluster we performed self-consistent KKR calculations in the full-potential approximation. The forces acting on Co adatoms and magnetic moments on atoms are obtained as the result of these calculations. We found that relaxations (shortening of the bond length and a reduction of the distance to the substrate) have no strong effect on the spin magnetic moments of Co clusters in contrast to the results for orbital moments and the magnetic anisotropy energy [6].

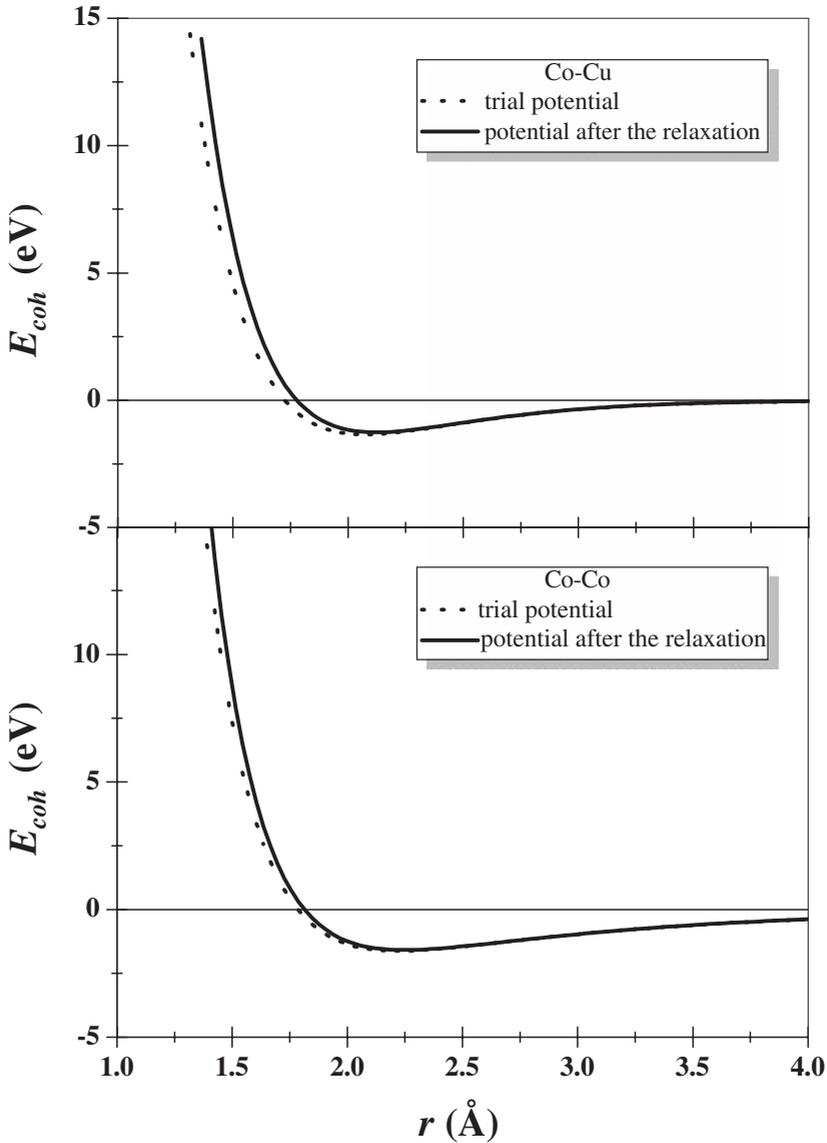
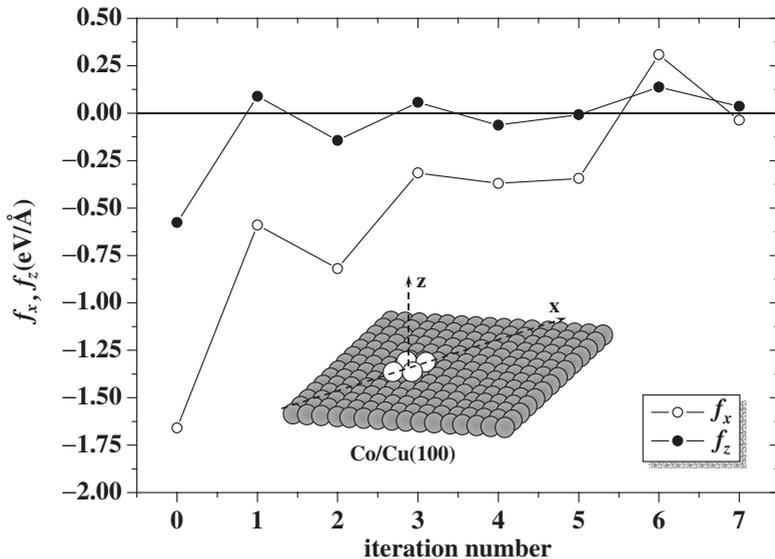


Figure 2. The potentials for Co–Cu and Co–Co interactions.

This is because the majority state of Co is practically filled. The effect of the substrate is mainly determined by the hybridization of the *sp* Cu states with the *d* states of the Co adatom. Our results show that the forces (vertical and horizontal) acting on Co atoms in the Co_4 cluster after relaxation with the trial potentials are not zero (see figure 3). We fitted potentials for Co–Cu and Co–Co interactions to accurately reproduce these forces. The cluster was again relaxed using new potentials, and *ab initio* calculations of forces and magnetic moments were again performed. We found that only seven iterations (at each iteration the potentials are fitted to the *ab initio* forces) are necessary to find the equilibrium structure of the cluster. The results presented in figure 2 show that the interatomic potentials, which nearly

Table 1. Bond lengths and vertical coordinates of the Co_4 cluster.

	Ideal	Trial potentials	<i>Ab initio</i>
r (Å)	2.56	2.38	2.30
z (Å)	0.00	-0.07	-0.05

Figure 3. Forces acting on atoms in the Co_4 cluster during relaxation. Variation in the vertical and horizontal forces is presented.

perfectly reproduce fully *ab initio* results, are very close to the trial potentials. It can be seen that it is mainly the short-range repulsive part of the potential that changes during relaxation. Our analysis shows that the electronic states and magnetic moments of clusters calculated for the relaxed structure obtained with the trial potentials (the first iteration, see figure 4) are similar to results for clusters relaxed fully *ab initio* (the last iteration, see figure 4). The bond length in the Co_4 cluster after *ab initio* relaxation is reduced by 0.08 \AA compared with the results using the trial potentials.

The above findings clearly demonstrate that the interatomic potentials constructed by fitting to an *ab initio* data pool can be used to determine the equilibrium structure of supported clusters. Even after the first iteration (the calculation with the trial potentials) the geometrical structure and the electronic and magnetic states are very similar to the results of fully *ab initio* calculations. We believe that, especially in the case of large supported magnetic clusters, our approach to the calculation of atomic relaxations and electronic states can be very useful. To the best of our knowledge, such calculations have not yet been performed.

We also used our method to determine the relaxed structure and magnetic moments of Co_2 , Co_5 and Co_9 clusters on an ideal $\text{Cu}(001)$ surface. Similar to the calculation for Co_4 , we needed only six to seven iterations to find the equilibrium structure for all clusters. Our results for the bond lengths and magnetic

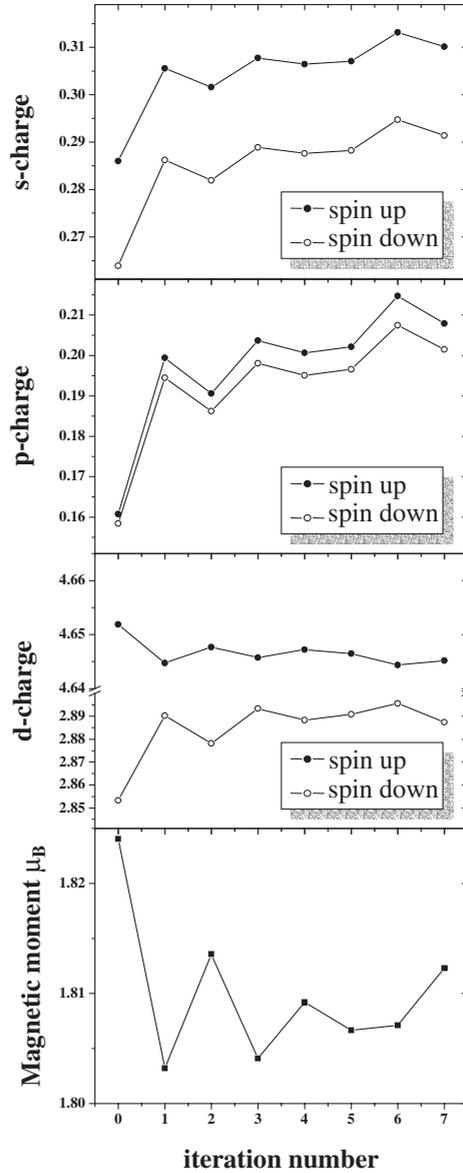


Figure 4. Changes in the charges in the WS cell and the local magnetic moments on atoms in the Co_4 cluster during relaxation.

moments are presented in Table 2. One can see that the trial potentials give a very good approximation to the geometrical and magnetic structure of the clusters.

4. Summary

Using the KKR Green's function method and an N -body potential constructed by fitting to *ab initio* results, we have developed a new method for *ab initio* relaxations of magnetic supported clusters. This approach allows us to find the

Table 2. Bond lengths, vertical coordinates and magnetic moments of Co₂, Co₅ and Co₉ clusters.

	Ideal	Trial potentials	<i>Ab initio</i>	
r (Å)	2.56	2.37	2.29	
z (Å)	0.00	-0.14	-0.12	
M (μ _B)	1.89	1.86	1.86	
$r_{1,2}$ (Å)	2.56	2.39	2.36	
z_1 (Å)	0.00	-0.10	-0.02	
z_2 (Å)	0.00	-0.03	-0.06	
M_1 (μ _B)	1.73	1.64	1.68	
M_2 (μ _B)	1.85	1.85	1.83	
$r_{1,2}$ (Å)	2.56	2.40	2.38	
$r_{1,3}$ (Å)	3.61	3.43	3.37	
z_1 (Å)	0.00	-0.02	0.05	
z_2 (Å)	0.00	-0.04	0.00	
z_3 (Å)	0.00	-0.06	-0.02	
M_1 (μ _B)	1.82	1.78	1.80	
M_2 (μ _B)	1.74	1.72	1.73	
M_3 (μ _B)	1.74	1.74	1.74	

geometry and the electronic and magnetic states of clusters fully self-consistently. We have demonstrated that only a few iterations should be performed in *ab initio* calculations to determine the structure and magnetic moments of small Co clusters on Cu(001).

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