Ab initio approach for atomic relaxations in supported magnetic clusters

V.S. Stepanyuk\textsuperscript{a,*}, A.L. Klavsyuk\textsuperscript{b}, L. Niebergall\textsuperscript{a}, A.M. Saletsky\textsuperscript{c}, W. Hergert\textsuperscript{b}, P. Bruno\textsuperscript{a}

\textsuperscript{a}Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany
\textsuperscript{b}Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany
\textsuperscript{c}General Physics Department, Moscow State University, 119899 Moscow, Russia

Abstract

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 of supported clusters. As an example, we present our results for small Co clusters on Cu(001). Changes in electronic and magnetic states of clusters due to atomic relaxations are revealed.

Key words: Ab initio calculations; tight-binding approximation; atomic relaxations.

* Corresponding author. E-mail: stepanyu@mpi-halle.de, Phone: +49 345 5525429, Fax: +49 345 5525446
1 Introduction

One of the central issues in physics of nanostructures is the interplay between atomic structure, electronic and magnetic states. Different empirical and semi-empirical potentials have been used to determine the interatomic interactions (Brenner, 2000). 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 an important results on 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. Several calculations of structural relaxations, electronic and magnetic properties of small magnetic clusters on metal surfaces have been recently performed using a quantum-chemical methods (Nayak et al., 2001). A metal surfaces in such calculations is approximated by the finite atomic cluster. One of the difficulties associated with using 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 have developed N-body interatomic potentials formulated in the second moment tight-binding approximation (TB-SMA) (Levanov et al., 2000). Parameters of potentials are fitted to accurate first-principle calculations of selected cluster-substrate properties. This scheme allows us to correctly reproduce bonding in transition metal clusters on metal surfaces. Several applications of our potentials can be found in recent publications (Levanov et al., 2000; Stepanyuk et. al., 2000; Stepanyuk et al., 2003; Tsivlin et al., 2003; Longo et al., 2004). 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 an semi-infinite metal substrates. Many-body potentials are used to approximate trajectories of atoms during the relaxation. Ab initio Helmmann-Feynman (HF) forces are calculated to find an equilibrium structure. Structure, 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 mag-
hetic properties (Wildberger et al., 1995; Papanikolaou et al., 1997). 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 the 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 being 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:

\[ G_{j,j'}^{ll'}(k, E) = G_{j,j'}^{ll'}(k, E) + \sum_{j''l''} G_{j,j''}^{ll''}(k, E) \Delta t_{j''}^{ll''}(E) G_{l''l'}^{j''j'}(k, E). \]  

(1)

Here \( \hat{G} \) is the structural Green’s function of the bulk in a \( k \parallel \)-layer representation (\( j, j' \)-layer indices). The \( k \parallel \) wave vector belongs to the 2D Brillouin zone. \( \Delta t_{j}^{ll}(E) \) 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:

\[ G_{n,n'}^{ll'}(E) = G_{n,n'}^{ll'}(E) + \sum_{n''l''} G_{n,n''}^{ll''}(E) \Delta t_{n''}^{ll''}(E) G_{l''l'}^{n''n'}(E), \]

(2)

where \( G_{n,n'}^{ll'}(E) \) is the energy-dependent structural Green’s function matrix and \( \hat{G}_{n,n''}^{ll''}(E) \) the corresponding matrix for the ideal surface, serving as a reference system. \( \Delta t_{n}^{ll}(E) \) 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 to the shifted coordinate system using the transformation matrix (Papanikolaou et al., 1997). 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 (Papanikolaou et al., 1997).

Many-body potentials are formulated in the second moment tight binding approximation (Levanov et al., 2000). 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 band energy and repulsive part:
\[
E_{\text{coh}} = \sum_i \left( E^i_R + E^i_B \right)
\]  
(3)

\[
E^i_R = \sum_j A_{\alpha\beta} \exp\left(-p_{\alpha\beta}\left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1\right)\right)
\]  
(4)

\[
E^i_B = -\left(\sum_j \xi_{\alpha\beta}^2 \exp\left(-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1\right)\right)\right)^{1/2}
\]  
(5)

\(r_{ij}\) is the distance between the atoms \(i\) and \(j\). \(r_{\alpha\beta}^0\) is the first neighbors distance in the crystalline structures of the pure metals for atom-like interactions and becomes an adjustable parameter in the case of the cross interaction. \(\xi\) is an effective hopping integral; \(p_{\alpha\beta}\) and \(q_{\alpha\beta}\) describe the decay of the interaction strength with distance of the atoms.

Binding energies of supported and embedded clusters of different sizes and geometry, the HF forces acting on adatoms and surface energies are accurately fitted to the ab initio results to find parameters of potentials. We should note that bonds of low coordinated atoms are considerably stronger than bonds in the bulk. Therefore, surface properties should be included in fitting 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 includes also such bulk properties as 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 (Levanov et al., 2000; Longo et al., 2004; Stepanyuk et al., 2004). Here, we show that these potentials can be used to perform a fully ab initio atomic relaxations by means of the KKR Green’s function method. The key idea of our approach is presented in Fig.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 as the trial ones. 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 zero, the potentials are fitted again to correctly reproduce these ab initio forces. The structure of the cluster is again relaxed with a new fitted potentials. We repeat calculations until ab initio forces are very small, i.e. the cluster is fully relaxed. We should note that, in fact, ab initio relaxations of supported clusters without using of potentials, are possible, however they require much more computational efforts. The problem is that any small changes in the position of some atom of the cluster during relaxation lead to strong changes in forces acting on different atoms. Ab initio fitted many-body potentials allow us to find a very good approximation for displacements of atoms at each iteration. In other words, potentials ‘help’ the ab initio method to find correct atomic displacements. We will show that
Fig. 1. Schematic presentation of the method for relaxations of supported clusters; KKR Green’s function method and ab initio fitted many-body potentials are used to determine structure, electronic and magnetic states in clusters fully self-consistently. Only 6-7 iterations should be performed to fully relax small magnetic clusters. 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 results for the Co$_4$ cluster. As the first application of the method, we present calculations for atomic relaxations in clusters on the ideal Cu substrate. The 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 very good approximation to the fully ab initio results. Therefore, we believe that reliable results for atomic relaxations in the substrate can be simply obtained using our potentials without performing a fully ab initio calculations (Stepanyuk et al., 2000; Tsivlin et al., 2003; Longo et al, 2004;)

In Fig. 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
Fig. 2. The potentials for Co-Cu and Co-Co interactions.

Table 1
The bond length and vertical coordinates of Co$_4$ cluster.

|        | ideal | trial potentials | ab initio |
|--------|-------|------------------|-----------|
| $r$(Å) | 2.56  | 2.38             | 2.30      |
| $z$(Å) | 0.00  | -0.07            | -0.05     |

have carried out the 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 unrelaxed ones by as much as 0.2 Å and 0.07Å correspondently.

For the relaxed structure of the Co$_4$ cluster we perform the 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 have found that relaxations(shortening of the bond length and decreasing of the distance to the substrate) has no strong effect on the spin magnetic moments of Co clusters in contrast to results for orbital moments and the magnetic anisotropy energy(Pick et al., 2003). 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 Co₄ cluster after the relaxation with the trial potentials are not equal zero, see Fig 3. We have fitted potentials for Co-Cu and Co-Co interactions to

Fig. 3. Forces acting on atoms in the Co₄ cluster during the relaxation; variation in the vertical and horizontal forces is presented. accurately reproduce these forces. The cluster was again relaxed using a new potentials, and ab initio calculations of forces and magnetic moments were again performed. We have found that only 7 iterations (at each iteration the potentials are fitted to the ab initio forces) are necessary to find the equilibrium structure of the cluster. Results presented in Fig.2 show that the interatomic potentials which nearly perfectly reproduce a fully ab initio results are very close to the trial potentials. It is seen that mainly the short-range repulsive part of the potential changes during the relaxation. Our analysis shows that electronic states and magnetic moments of clusters calculated for the relaxed structure obtained with the trial potentials (the first iteration, see Fig.4) are close to results for clusters relaxed fully ab initio (the last iteration, see Fig.4). The bond length in the Co₄ cluster after the ab initio relaxations is reduced by 0.08 Å compared to results with 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 an
equilibrium structure of supported clusters. Even after the first iteration (the calculation with the trial potentials) the geometrical structure, electronic and magnetic states are very close to the results of fully ab initio calculations. We believe that, especially in the case of large supported magnetic clusters, our approach for calculations of atomic relaxations and electronic states can be very useful. To the best of our knowledge such calculations have not been performed yet.

We have also used our method to determine the relaxed structure and magnetic moments of Co$_2$, Co$_5$ and Co$_9$ clusters on the ideal Cu(001) surface.
Table 2
The bond lengths, vertical coordinates and magnetic moments of Co₂, Co₅ and Co₉ clusters.

| Cluster | Ideal | Trial Potentials | Ab Initio |
|---------|-------|------------------|-----------|
| Co₂     |       |                  |           |
| r(Å)    | 2.56  | 2.37             | 2.29      |
| z(Å)    | 0.00  | -0.14            | -0.12     |
| M(µB)   | 1.89  | 1.86             | 1.86      |
| Co₅     |       |                  |           |
| r₁,₂(Å) | 2.56  | 2.39             | 2.36      |
| z₁(Å)   | 0.00  | -0.10            | -0.02     |
| z₂(Å)   | 0.00  | -0.03            | -0.06     |
| M₁(µB)  | 1.73  | 1.64             | 1.68      |
| M₂(µB)  | 1.85  | 1.85             | 1.83      |
| Co₉     |       |                  |           |
| r₁,₂(Å) | 2.56  | 2.40             | 2.38      |
| r₁,₃(Å) | 3.61  | 3.43             | 3.37      |
| z₁(Å)   | 0.00  | -0.02            | 0.05      |
| z₂(Å)   | 0.00  | -0.04            | 0.00      |
| z₃(Å)   | 0.00  | -0.06            | -0.02     |
| M₁(µB)  | 1.82  | 1.78             | 1.80      |
| M₂(µB)  | 1.74  | 1.72             | 1.73      |
| M₃(µB)  | 1.74  | 1.74             | 1.74      |

Similar to the calculation for the Co₄, we needed only 6-7 iterations to find the equilibrium structure for all clusters. Our results for the bond lengths and magnetic moments are presented in Table 2. One can see that the trial potentials give a very good approximation for the geometrical and magnetic structure of clusters.

4 Summary

By using the KKR Green’s function method and an N-body potentials 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 geometry, electronic and magnetic states in 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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