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Theoretical study of the charge transfer in supported transition metal microclusters

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Abstract. The validity of the local charge neutrality approximation within the tight-binding method has been benchmarked against the global charge neutrality approximation. Calculations have been performed for Fe microclusters supported on the Ni(001) surface using a self-consistent *spd* tight-binding method parametrised to ab initio tight-binding linear muffin-tin orbital results. In order to enhance the effect of the hybridisation between both elements, we have considered an artificial strong interfacial relaxation of the geometries which were predicted by means of molecular dynamics calculations. Our results confirm the validity of the local charge neutrality approximation when a careful parametrisation is used and appropriate values for the charge in each site are elected.

PACS. 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 75.75.+a Magnetic properties of nanostructures

1 Introduction

In the last few years, the study of supported transition metal nanostructures has attracted a lot of attention due to the technological interest of these systems. However, neither the experimental nor theoretical studies of them are easy. On the theoretical side, the fact of being extended systems where the symmetry is broken restricts the use of ab initio methods, such as those based on the density-functional theory (DFT), due to the high computational cost that these problems require. In this context, the use of semiempirical methods can provide a good degree of accuracy while keeping the computational demands at a reasonable level. Among the semiempirical methods, the self-consistent real space tight binding (TB) model has been successfully used in the study of these kind of systems. For example, in recent works we have studied Ni and Fe clusters at the Al(001) surface [1,2]. However, the computational cost is not the only problem that arises. One of the biggest issues is the charge transfer. This is always true when investigating the magnetic and electronic properties of transition metal clusters in presence of surfaces or interfaces. In the case of supported nanostructures, both a surface and an interface are present and the appropriate treatment of the charge transfer becomes particularly important. In this work we will discuss two different approaches within the TB method. To compare them we have performed calculations in Fe microclusters supported on the Ni(001) surface, which have recently been studied by Lau et al. [3] using X-ray magnetic circular dichroism. This is a non trivial system due to the presence of Fe, which is BCC in the bulk configuration, on a FCC substrate, as it is Ni. In Section 2 we discuss the theoretical model and the approximations which have been used. In Section 3 we present and discuss our results, and in Section 4 we summarise our main conclusions.

2 Theoretical model

In the TB method the magnetic and electronic properties are determined by self-consistently solving a TB Hamiltonian for the s, p and d valence electrons in a mean-field approximation using the recursion method [4]. In the usual notation of second quantisation, the real space Hamiltonian H is given by

$$H = \sum_{i,\alpha,\sigma} \epsilon_{i\alpha\sigma} N_{i\alpha\sigma} + \sum_{\substack{\alpha,\beta,\sigma \\ i\neq j}} t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma}, \qquad (1)$$

where $c_{i\alpha\sigma}^{\dagger}$ ($c_{j\beta\sigma}$) is the operator for the creation (annihilation) of an electron with spin σ and orbital state α (β) at the atomic site i (j), and $N_{i\alpha\sigma}$ is the number operator. Electron delocalisation within the system is described by

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the hopping integrals $t_{ij}^{\alpha\beta}$, which we included up to the second neighbours and assumed to be spin-independent. The heteronuclear hoppings were calculated as the average of the corresponding homonuclear hoppings. The spin-dependent diagonal terms $\epsilon_{i\alpha\sigma}N_{i\alpha\sigma}$ include electron-electron interaction through a correction of the energy levels. This energy levels, $\epsilon_{i\alpha\sigma}$, adopt a different expression within the local charge neutrality approximation (LCNA) and the global charge neutrality approximation (GCNA).

The LCNA was first introduced in research on surfaces and interfaces by Victora and Falicov [5]. In this approximation the charge in each site is fixed to given results. In order to fulfil this request, adjustable site- and orbital-dependent potentials ($\Omega_{i\alpha}$) should be introduced, obtaining the next expression for the energy levels:

$$\epsilon_{i\alpha\sigma} = \epsilon_{i\alpha}^{0} - z_\sigma \frac{1}{2}\sum_{\beta} J_{i\alpha\beta}\mu_{i\beta} + \Omega_{i\alpha}, \tag{2}$$

where $\epsilon_{i\alpha}^{0}$ is the bare energy of orbital α at site i (that is, excluding Coulomb interactions), and the second term is the correction for spin polarisation of the electrons at site i ($\mu_{i\beta} = \langle N_{i\beta\uparrow}\rangle - \langle N_{i\beta\downarrow}\rangle$, that is, the local magnetic moment excluding the orbital part). In this second term, the $J_{i\alpha\beta}$ are the exchange integrals and z_σ is the sign function ($z_\uparrow = +1$; $z_\downarrow = -1$). The $\Omega_{i\alpha}$ potentials are modified during the self-consistent procedure in order to recover the required charge on each site.

In the GCNA charge transfer is allowed between different sites and orbitals. Only the total charge of the system is fixed. In order to control the charge transfer, the variations on the local environment must be reflected in shifts of the energy level. We can see how in the expression for the energy levels within the GCNA:

$$\varepsilon_{i\alpha\sigma} = \varepsilon_{i\alpha}^{0,at} + Z_i\xi_{i\alpha} + \sum_{\beta} U_{i\alpha\beta}N_{i\beta} - z_\sigma \frac{1}{2}\sum_{\beta} J_{i\alpha\beta}\mu_{i\beta}. \tag{3}$$

Here, $\varepsilon_{i\alpha}^{0,at}$ is the bare energy of orbital α at site i for the isolated atom; $Z_i\xi_{i\alpha}$ is the crystal field potential, Z_i being the local atomic coordination; and $U_{i\alpha\beta}$ is the Coulomb integral. By including the crystal field potential, the local geometrical variations of the environment are taken into account (i.e. the presence of a surface). By including the third term in equation (3) the local chemical variations of the environment are considered (i.e. the presence of an interface). The total charge of the system is recovered at each iteration by moving the Fermi level.

In both approximations, several parameters must be chosen. The $\epsilon_{i\alpha}^{0}$ levels in the LCNA, the homonuclear hopping integrals $t_{ij}^{\alpha\beta}$ and the exchange integrals $J_{i\alpha\beta}$ have been determined from a fit to TB linear muffin-tin orbital (TB-LMTO) [6] results of a single system, which is an Fe monolayer on top of the Ni(001) surface. From this system we have also taken the values of the charge for each site in the LCNA. The election of the system is due to the fact that, as the clusters, the Fe monolayer on top of the Ni(001) surface presents an interface between both metals and the Fe atoms are on top of the Ni(001) surface. In this way, the effects of the geometrical and chemical variations of the environment are implicitly taken into account in the election of the parameters indicated above and in the values of the charge that will be fixed in the LCNA. This procedure has been successfully used in previous works [2,7,8]. For the GCNA there are more parameters to be determined. The Coulomb integrals $U_{i\alpha\beta}$ have been taken from a previous work [9]. For transition metals they are close to the limit $U \to \infty$. In practise, this fact implies that the charge transfer will not be large; thus, the GCNA results will not be very different from the LCNA ones (as we will see below). The bare energy levels $\varepsilon_{i\alpha}^{0,at}$ and the crystal field parameters $\xi_{i\alpha}$ are unique for each material and have been determined from a series of TB-LMTO calculations of Fe and Ni systems with different coordinations.

As indicated in Section 1, Fe clusters on the Ni(001) surface have recently been studied by Lau et al. [3]. In this work, the authors interpret their measurements as derived from two-dimensional configurations for the Fe clusters, following a pseudomorphic arrangement on the Ni surface. To theoretically confirm this interpretation, we have determined the lowest-energy structures of the supported Fe$_n$ clusters with $2 \le n \le 9$ by combining the modified embedded atom model (MEAM) [10–12] with quenched molecular-dynamics simulations. The procedure was similar to that used in reference [2] for the study of Fe$_n$ clusters at the Al(001) surface. Our structural calculations predict that the most stable structures of the supported Fe$_n$ clusters are planar configurations, as suggested in the experimental work by Lau et al. [3]. The obtained cluster geometries and interatomic distances were used to perform the electronic structure calculations. However, in order to enhance the effect of the hybridisation between both elements, we have considered an artificial Fe-Ni inward relaxation of 20% with respect to Ni-Ni distances, whereas the MEAM calculation predicted an outward relaxation of 4%. In this way, the less favourable conditions for the charge transfer are considered in the comparison between GCNA and LCNA.

3 Results and discussion

Following the theoretical method described above, we have performed spin-polarised electronic structure calculations for Fe$_n$ clusters on top of the Ni(001) surface, with $2 \le n \le 9$. Calculations were done using both the LCNA and GCNA. In both cases, we obtained the occupations and magnetic moments per atom for the Fe cluster, which are shown in Figure 1. In the LCNA the charge has been chosen to be the same for all cluster sizes. Its value has been taken from the Fe monolayer supported on Ni(001), calculated by means of the TB-LMTO ab initio model. This value of the occupation is $7.59e^-$ per Fe atom. In the GCNA the evolution of the charge transfer from the smaller to the bigger clusters can be seen. The highest charge transfer is obtained for the smallest cluster (the 2 atoms one). In this case, the value of the charge is $7.20e^-$ per Fe atom. If the value of Fe bulk is taken as

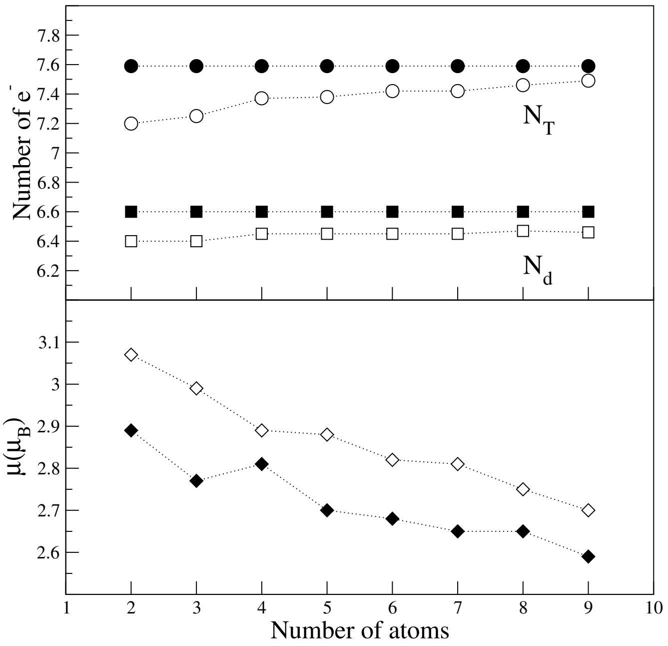

Fig. 1. Number of electrons (upper panel) and magnetic moment (lower panel) per atom of Fe_n clusters ($n = 2{-}9$) supported on Ni(001), as function of n. Filled symbols correspond to LCNA calculations and open circles to GCNA calculations. In the upper panel, circles represent total occupations and squares d occupations. Lines joining points and merely visual aids.

reference, the charge transfer in this case is $0.80e^-$, which can be compared with the $0.41e^-$ in the LCNA. This is not a small value, but several facts must be considered. On the one hand, this is the less favourable case. For this cluster size only one of the first-nearest-neighbours of the Fe atoms is also Fe, being all the rest Ni atoms. Therefore, the changes in the local environment due to chemical reasons are the biggest. On the other hand, we have introduced a big artificial inward relaxation which enhances the hybridisation between both elements. Besides, despite the relatively important difference in the charge transfer, the magnetic moment do not change as much as it could do. A difference of roughly $0.4e^-$ in the charge could lead to a difference of more than $0.5\mu_B$ in the magnetic moment. However, as can be seen in Figure 1, the difference in the magnetic moment is only $0.18\mu_B$. We must also remember that d electrons are the most important ones to explain the magnetic properties of transition metals. For Fe_2 the d-occupation in the LCNA is $6.60e^-$, while within the GCNA is $6.40e^-$. The difference is half that found for the total occupation and this fact also helps to understand the relatively small difference in the magnetic moment.

If we focus now in the evolution of the results with the cluster size, we can see that, as the size of the cluster increases, the charge transfer decreases, until a value of $0.51e^-$ is obtained for the 9-atom cluster. This charge transfer is already close to the LCNA one. This fact can be understood if we take into account that, if two-dimensional configurations are assumed, the natural limit of the planar clusters is the monolayer and this is the system from where the value of the occupation in the LCNA was taken.

Regarding the magnetic moments, a decrease can be observed as the cluster size increases. This can be easily related to the increase in the coordination of the supported clusters as its size increases. For the whole series, the magnetic moments obtained within the GCNA are slightly bigger (between 0.1 and $0.2\mu_B$) than that obtained within the LCNA. This is consistent with the fact that increasing the occupation of a more than half filled d-band tends to reduce its magnetic moment. The difference in the magnetic moment between LCNA and GCNA can also be related to the difference in d-occupation, which also remains between 0.1 and $0.2e^-$.

It is then clear than the use of the LCNA implies a loss in the accuracy. However, this loss can be controlled even in the less favourable situation, which is the case studied here. In general, we can conclude that the LCNA leads to results which are consistent with those obtained with the GCNA and which allow to achieve the same qualitative conclusions. At this point, we must remember than TB methods always give qualitative more that quantitative answers, but with the advantage of being able to treat systems which can not be treated with more accurate methods, like those based on DFT.

Finally, it is worth to discuss when the GCNA or the LCNA should be used. The GCNA is more accurate, but in order to use it more parameters must be determined. The higher number of parameters implies more tests to be done and therefore more time and effort are needed in order to get an answer. The LCNA is less accurate, but it implies less parameters and all of them can be determined from a single fit. However, within this approximation a very strong constriction is imposed. Due to this fact, the self-consistence can be extremely difficult to achieve, leading to oscillatory behaviours that can not be easily overcome. In practise, that makes this approximation impossible to be used in certain cases, like non-collinear calculations. In this cases, the GCNA must be employed.

4 Conclusions and perspectives

In this work we have benchmarked the validity of the LCNA against the GCNA by performing self-consistent *spd* TB calculations using both approximations. As test system we have used planar Fe clusters on the Ni(001) surface. We have obtained the most stable geometries using the MEAM. In order to enhance the hybridisation, we have included an artificial inwards relaxation of the Fe-Ni distances. We have seen that both approximations lead to the same qualitative conclusions even in the less favourable conditions. Finally, we have discussed which are the advantages and the disadvantages of each approximation. A systematic study of Fe clusters on Ni(001) is in progress and will be published in the near future.

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