Embedding method to simulate single atom adsorption: Cu on Cu(100)

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Abstract. Within full relativistic four-component *ab initio* density functional calculations we examined the adsorption of a Cu adatom on a Cu(100)-surface. The surface was simulated by a cluster of Cu atoms in which the number of atoms was successively increased to 99 atoms. Through extensive studies we were able to get convergence in adsorption energy and bond distance with about 60 atoms. Using converged cluster sizes, the results of the binding characteristics are in good agreement with other solid-state calculations. The same adsorption process was then studied with much smaller clusters that were embedded into different types of environments. By this scheme we were able to reproduce the same converged results with a decreased cluster size of only about 25 embedded atoms.

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1 Introduction

Nearly 90% of all chemical products are generated by catalytic reactions where an atom or molecule enhances its reactivity due to the adsorption on a surface. This causes an immense interest in the theoretical understanding of surface processes and their nature.

For the understanding of adsorption processes the knowledge of the interaction between the adatom and the surface is indispensable. In contrast to many solid-state properties the adsorption process is a local phenomenon. A number of ways exist for calculating surface quantities with solid-state methods, however there are very few molecular-based approaches where the cluster-size convergence is achieved.

For semi-conductor and insulator systems, it has been practical to study surface reactions using both periodically infinite 2-dimensional slabs and finite clusters. Here the slabs have been useful for comparing to experiments on ordered overlayers and the clusters to examine details of the reaction mechanism itself. Such cluster approximations can provide a good description of surface reactions because the surface states tend to be fairly localized (with penetration into the bulk dropping off at a rate related to the band gap). Part of the slow progress in describing processes on metallic surfaces is the delocalization of the valence electrons which is characteristic for good metals. Consequently, it is still uncertain how well finite clusters

(and thin slabs) can describe the reactions of semi-infinite surfaces.

Since accurate simulations of metal surfaces by clusters usually require a large amount of atoms, we developed an embedding scheme where a relatively small cluster is embedded into an environment. By applying this approach, the number of atoms that are treated fully self-consistently could be decreased enormously. Due to the cubic relation between the number of atoms and the calculation time, the embedding scheme allows to study processes on extended clusters on reasonable time scales.

In the next section we briefly explain the embedding method and how to determine the properties of the environment. Then, we examine the adsorption of copper on Cu(100) without the embedding method to obtain cluster-size converged values, which were attempted to be reproduced with smaller embedded systems.

2 Method

The embedding scheme is based on a relativistic four-component self-consistent field density functional approach. Details of this method have been reported several times [1–4]. During the self-consistent cycles for calculating the total energy of the system, the exchange-correlation functional is given by the relativistic local-density approximation (rLDA) [5,6] within the parameterization for the correlation suggested by Vosko, Wilk, and Nusair [7]. Nonlocal corrections are calculated

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perturbatively with the relativistic forms of the generalized gradient approximation (rGGA) [8]. For the exchange we use Becke's [9] formulation, and for the correlation the functional proposed by Perdew [10] (B88/P86). This fully self-consistent approach was applied to all calculations to obtain cluster-size converged results. These examinations will be discussed in Section 3.1.

The method that was applied to calculations in which the cluster is embedded into an environment has been described in [4,11,12] but will be explained here briefly.

For DFT approaches the most important ingredient is the electronic density. If one expresses the total electronic density $\varrho(\boldsymbol{r})$ of a large cluster by a sum of atomic radial densities $F_k^r(\xi_k)$:

$$\varrho(\boldsymbol{r}) \approx \widetilde{\varrho}(\boldsymbol{r}) = \sum_{k=1}^{N} \sum_{r=1}^{M_k} \sum_{l=0}^{L_r} \sum_{m=-l}^{l} Q_{rm}^{kl} F_k^r(\xi_k) Y_l^m(\theta_k, \phi_k), \quad (1)$$

then the whole system can be divided into two parts. The *inner cluster* and the *environment*. The inner cluster consists of atoms that are located near the adsorbate, while the rest forms the environment. The same separation that was done for the density:

$$\widetilde{\varrho}(\boldsymbol{r}) = \widetilde{\varrho}_{\mathrm{cl}}(\boldsymbol{r}) + \widetilde{\varrho}_{\mathrm{env}}(\boldsymbol{r}) \quad (2)$$

can be done with the Coulomb potential. Following the derivation proposed in references [4,11] the partitioning of the system leads to the following expression for the total energy of the inner cluster under the influence of an external potential V_{env} formed by the environmental atoms

$$\begin{aligned} E_{\mathrm{tot}} &= E_{\mathrm{cl}} + \sum_{i=1}^{M_{\mathrm{cl}}} \langle \psi_i | V_{\mathrm{env}}(\boldsymbol{r}) | \psi_i \rangle \\ &= \sum_{i=1}^{M_{\mathrm{cl}}} n_i \, \varepsilon_i - \frac{1}{2} \int \left(V_{\mathrm{cl}}^{\mathrm{C}} + V_{\mathrm{env}}^{\mathrm{C}} \right) \varrho^{\mathrm{cl}} \, \mathrm{d}^3 r \\ &+ \sum_{\nu=1}^{N_{\mathrm{cl}}} Z_\nu \left(V_{\mathrm{env}}^{\mathrm{N}}(\boldsymbol{R}_\nu) + V_{\mathrm{env}}^{\mathrm{C}}(\boldsymbol{R}_\nu) \right) + E^{\mathrm{xc}} \\ &- \int \left(V_{\mathrm{cl}}^{\mathrm{xc}} + V_{\mathrm{env}}^{\mathrm{xc}} \right) \varrho^{\mathrm{cl}} \, \mathrm{d}^3 r + \frac{1}{2} \sum_{\substack{\nu,\mu=1 \\ \nu \neq \mu}}^{N_{\mathrm{cl}}} \frac{Z_\nu Z_\mu}{|\boldsymbol{R}_\nu - \boldsymbol{R}_\mu|}. \end{aligned} \quad (3)$$

Here the indices M_{cl} and N_{cl} go over the electrons and nuclei of the inner cluster, respectively. The influence of the environment is also included in the energy eigenvalues ε_i and the eigenfunctions ψ_i.

Since the properties and the quality of the environment are determined by the atomic densities that are located at the centers of the environment, we used three different schemes to create these densities before examining the adsorption on the embedded system:

- *neutral:* the density of a neutral, free atom;
- *SCF:* one fully self-consistent large cluster calculation is performed. In the following embedded system calculation every center of the environment gets the atomic density corresponding to its location in the large cluster calculation (see Ref. [12]);

- *bulk:* this kind of environment is most adapted to the real system. Within a preceding calculation of an embedded system (in all three directions) the averaged atomic density of the inner cluster atoms is copied to all centers of the environment after each iteration. If convergence is achieved, the final atomic density is a kind of *bulk density*.

After the calculation of the corresponding type of environmental densities, the densities are kept fixed. Afterwards, the process (here adsorption) is calculated on the embedded system.

3 Results and discussion

In this paper we studied the adsorption of atomic Cu on Cu(100), which is difficult to be simulated by clusters. This difficulty arises from the fact that copper is a very good conductor, which means the conductance electrons are strongly delocalized. Moreover, copper is a fairly heavy element, but nevertheless non-relativistic methods still can be applied. Therefore, we can compare our results with non-relativistic values to check the validity of the embedding method.

Instead of comparing the results for adsorption energy and bond distance with other methods, we wanted to be consistent within our method. Therefore, we calculated the copper adsorption on clusters without any environment first and then increased the amount of atoms until the values converged. Afterwards we embedded the smaller clusters into a specific environment and recalculated the adsorption energy and bond distance for comparison to previously obtained results.

In all calculations an atomic basis set consisting of $1s$–$4p$ wavefunctions ($3d$ included) was employed for atoms that were treated fully self-consistently.

3.1 Cluster expansion without environment

For the examinations of cluster-size convergence without any environment, we increased the amount of atoms until the values converged [17]. The different systems were: Cu–Cu$_4$, Cu–Cu$_{4.5}$, Cu–Cu$_{12.9.4}$, Cu–Cu$_{16.13.12.1}$, Cu–Cu$_{16.21.12.5}$, Cu–Cu$_{24.21.16.9}$, and Cu–Cu$_{32.25.24.13.4}$. A model of the largest system is shown in Figure 1.

With each system, we calculated the potential energy curve (see Fig. 2). The corresponding values for adsorption energy and bond distance are given in Table 1.

By comparing all curves it is apparent that there is a fluctuation in the values of the bond characteristic when the surface is simulated with < 71 atoms. The difference in bond distance and adsorption energy is only about 0.1 units between Cu–Cu$_{16.21.12.5}$ and Cu–Cu$_{24.21.16.9}$. This led to the conclusion that about 60 atoms are enough for modeling. Higher accuracy (≤ 0.1) can be achieved with the 71 atom cluster Cu–Cu$_{24.21.16.9}$. The final results in rLDA-approximation are: $-2.70 \, \mathrm{eV}$ and $3.35 \, \mathrm{a.u.}$ The corresponding GGA-value

Table 1. Binding energies and distances (only rLDA) for all calculated systems. The adsorption energies that are calculated within the rLDA- and B88/P86-functional are printed. Additionally the vibrational frequencies of the adsorbate are given that were calculated by fitted Morse potentials (the error is maximum 5%).

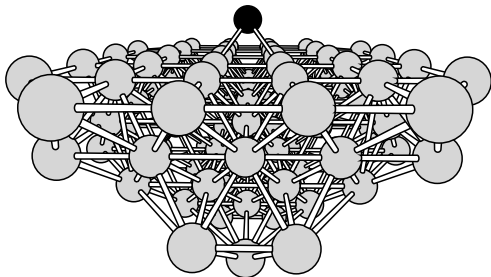| System | Adsorp. energy [eV] | | Bond dist. [a.u.] | Vib. freq. [cm^{-1}] |
	rLDA	B88/P86	rLDA	rLDA
Cu–Cu$_4$	−3.60	−2.55	2.70	165
Cu–Cu$_{4.5}$	−3.52	−2.64	2.95	166
Cu–Cu$_{12.9.4}$	−2.75	−1.84	2.95	153
Cu–Cu$_{16.13.12.1}$	−3.18	−2.46	3.20	154
Cu–Cu$_{16.21.12.5}$	−2.59	−1.68	3.25	153
Cu–Cu$_{24.21.16.9}$	−2.70	−1.79	3.35	154
Cu–Cu$_{32.25.24.13.4}$	−2.70	−1.79	3.34	154
Pentcheva [13]	−2.84			
Shin [14]	−2.74		3.15	
Kürpick [15]	−2.91		3.08	
[16]	−2.80		2.97	

Fig. 1. Model of the system Cu–Cu$_{32.25.24.13.4}$. The adsorbate (dark) is placed at the four-fold site on the surface (grey). In lateral direction the third nearest neighbors are included, and in vertical direction the cluster spans over 5 layers.
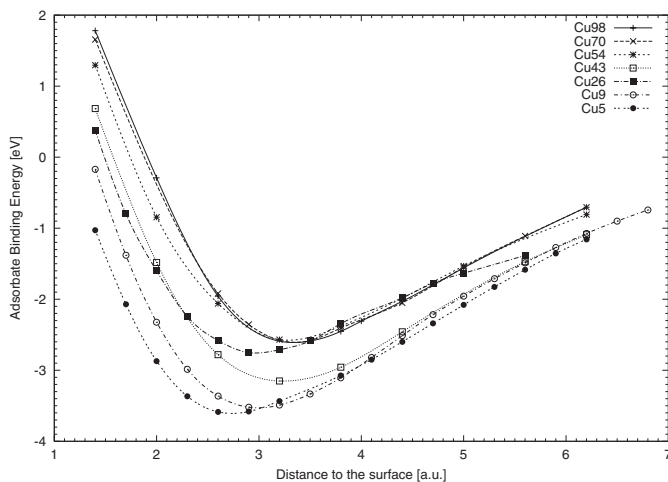

Fig. 2. Potential energy curves for the cluster-size converged calculations of the systems without environment.

for the energy is −1.79 eV whereas the bond distance is nearly the same as for rLDA. We checked the convergence with the next larger system Cu–Cu$_{32.25.24.13.4}$ (98 atoms) and obtained the same results which will be denoted as "converged values" in the following.

Since the shapes of all potential energy curves are nearly the same around the minima there are less fluctuations in the vertical vibrational energy of the adsorbate. The converged value was found to be 154 cm^{-1}.

It should be noted that a single value of the potential energy curve of the larger systems took about 9 months to be calculated on a common workstation (650 MHz). Only with the use of a heavy parallelization of the code was it possible to get all different curves.

3.2 Embedded cluster expansion

After the calculations of the converged values without environment were, performed similar studies were done for some of the smaller clusters which were embedded in an environment. The embedded systems are Cu–Cu$_4$, Cu–Cu$_{4.5}$, and Cu–Cu$_{12.9.4}$. For the atomic densities of the surrounding we applied all the different schemes: neutral, SCF, and bulk. All results for the adsorption energy and bond distance are given in Table 2.

As expected, the four atom embedded cluster is much too small to simulate the surface. For all types of environment the adsorbate is not bound. The behavior when different if a second layer is introduced to the inner cluster. By using the neutral or bulk environment there is no change, the adsorbate is still not bound. However, with the SCF environment that is mostly adapted to a large cluster the adsorbate is bound by −3.10 eV, and the distance from the surface is 3.87 a.u. If the 25 atom cluster Cu–Cu$_{12.9.4}$ is embedded, the adsorbate is bound with all three types of environment. The corresponding potential energy curves for this system are shown in Figure 3.

Within the most simple environment (neutral) the difference to the converged values is only 0.13 eV in energy and 0.03 a.u. in distance. The results using the SCF environment are similar, although the deviation in adsorption energy is only 0.07 eV. The comparison of the potential energy curves with neutral and SCF environment shows compatible shapes. The behavior within the bulk type environment, which is most adapted to the infinite system,

Table 2. Results for the embedded systems with all three environments. For comparison only the rLDA-results are listed. The values denoted as "this work" are for Cu–Cu$_{32.25.24.13.4}$ without environment.

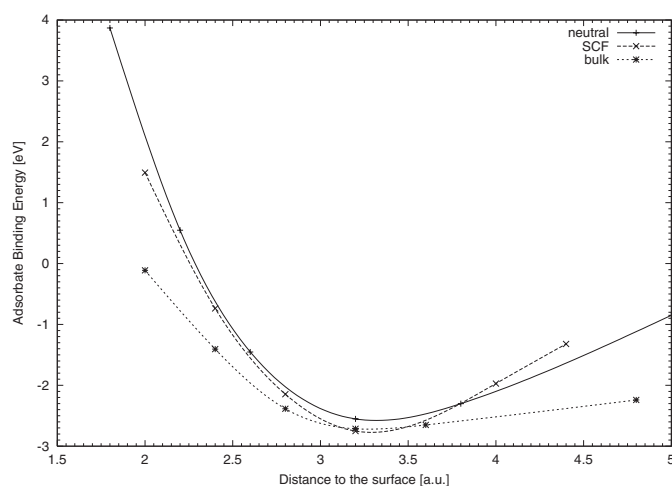| System	Env. occ.	Adsorp.-energy [eV] rLDA	Bond dist. [a.u.] rLDA
Cu–Cu$_4$	neutral	not bound	–
Cu–Cu$_4$	SCF	not bound	–
Cu–Cu$_4$	bulk	not bound	–
Cu–Cu$_{4.5}$	neutral	not bound	–
Cu–Cu$_{4.5}$	SCF	−3.10	3.87
Cu–Cu$_{4.5}$	bulk	not bound	–
Cu–Cu$_{12.9.4}$	neutral	−2.57	3.31
Cu–Cu$_{12.9.4}$	SCF	−2.77	3.30
Cu–Cu$_{12.9.4}$	bulk	−2.71	3.29
this work	without	−2.70	3.34
Pentcheva [13]		−2.84	
Shin [14]		−2.74	3.15
Kürpick [15]		−2.91	3.08
[16]		−2.80	2.97

Fig. 3. Potential energy curves for the adsorption on the embedded Pt$_{12.9.7}$ cluster with different types on environment.

is different. The shape of the curve is different from the others (see Fig. 3), however the values near its minimum are in very good agreement with the converged values. The calculated adsorption energy is −2.71 eV, and the bond distance is 3.29 a.u., which means that the differences to the converged values are only about 0.01 eV in adsorption energy and about 0.05 a.u. in bond distance. Comparing all results from the embedded systems, the Cu–Cu$_{12.9.4}$ led to the best results with all three types of environment. The bulk environment is only required for accuracy better than 0.1 in the bond properties.

4 Conclusion

In this paper we used a cluster method to examine the adsorption of a copper atom on the Cu(100) surface. Since surfaces are mostly treated by periodic methods like slab-calculations or other cluster methods, we wanted to be internally consistent. Therefore, we studied the adsorption of the Cu atoms on different sized clusters to get converged values within our fully relativistic approach first. Then, we showed that a surface-cluster which consists of about 50–60 atoms is sufficient to describe the adsorption process. It seems that most of all electronic relaxation effects of the surface introduced by the adsorbate are included in these clusters. After we obtained the converged values, we tried to reproduce these results with much smaller clusters that were embedded into an environment. If the embedded cluster had a size of about 25 atoms the results were in good agreement with the converged values we obtained without environment. This behavior is equivalent to the adsorption of an Al atom on Al(100) previously studied [4]. It seems that in general, metal surfaces which normally require large cluster sizes can be simulated by about 25 embedded atoms, but of course, this needs further investigations. We already started examining the adsorption of an O atom on Pt(111) surfaces. This case is more interesting than the homo-atomic systems since oxygen is a very reactive element that strongly disturbs the electronic density of the surface. For this process we found that a 28 atom Pt-cluster is sufficient to describe all possible adsorption sites: three-fold (hcp, fcc), bridge, on top [18]. With this knowledge we can start to examine surface reactions on platinum surfaces.

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