

Cluster-embedding method to simulate large cluster and surface problems

T. Jacob^a, B. Fricke, J. Anton, S. Varga, T. Baştuğ, S. Fritzsche, and W.-D. Sepp

Fachbereich Physik, Universität Kassel, Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

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Abstract. In order to describe processes which are localized on a surface or inside the bulk of a solid, molecular calculations of an inner cluster may be adequate as long as the effect of the outer environment is taken into account *via* an embedding-method. Using a relativistic density functional method for the self-consistent cluster calculation we have developed a new cluster-embedding scheme here. As an example we have studied the adsorption of Al on an Al(100) surface and we get significant agreement with different methods. This indicates that this embedding-method is reliable enough to simulate an unlimited solid.

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1 Introduction

From a very general point of view a solid is nothing but a big molecule. At first glance this seems to be a purely academic statement. Due to the fact that several processes like single atom/molecule adsorption or single impurities are localized phenomena it becomes clear that a molecular approach may be a good starting for a theoretical description. In such a cluster approach the surface or the inner part of a solid is simulated by a small number of atoms. If we include more and more atoms the description will become more accurate. However, the calculation-time and computer-memory request increases very fast with greater systems. Therefore, very soon any real calculation reaches its practical limits.

Thus, the question is: how large should the cluster be chosen in order to describe the problem properly? In some cases, depending on the system, convergence in bond energy or bond distance is achievable only with huge systems [1,2] whose calculations are too complex. Therefore we need approximations to calculate only a smaller part of the whole system self-consistently (*cluster*) and to simulate the auxiliary influences formed by the *environment*. One way that is suitable for our calculations is the embedding-method in which an inner cluster is calculated with the external potential of the environmental atoms. In literature one can find different realizations. One of the most popular methods to study adsorption on metal surfaces using an embedding cluster model was proposed by Whitten and Pakkanen [3]. They made a calculation of a large cluster and afterwards they used the obtained set of molecular orbitals (MO) to construct the external potential.

Based on this method Duarte and Salahub [4] added some more features. Having performed the time-consuming large cluster calculation they divide the system in three parts. Then they generate the external potential using the MOs localized in the outer region which they get by a method of Foster and Boys [5]. This minimizes the overlap between the inner and the two outer parts. Again this procedure is very time-consuming and limits its application. In addition deficiencies of the method are corrected by use of the experimental thermodynamic potential [6].

Another method was proposed by Song *et al.* [7]. They also divide the whole system in several parts. From the inner region the atomic potentials are “copied” (a procedure that will be explained in section 3.2) onto the surrounding atoms. The remaining atoms are simulated by point charges. Between the intermediate region and the point charges they put a pseudo-potential that is fitted to the bulk behaviour and guarantees charge conservation during the copy process. However, in most cases this procedure is only suitable to describe bulk properties.

But there are also methods that are based on a Green’s function formalism. Fukunishi and Nakatsuji [8] use an iterative procedure which is based on a restricted Hartree-Fock (RHF) approximation [9] to perform the embedding scheme.

Our first approach to simulate bulk and surface properties was to use full-relativistic cluster calculations and to look for the convergence with increasing cluster size [10, 11]. Due to computer time and memory this procedure very quickly reaches its practical limit. We therefore developed in this paper an embedding procedure which has the advantage that we neither need any fit parameters nor any full size calculations.

^a e-mail: timojaco@physik.uni-kassel.de

2 Method

The relativistic self-consistent field method which we use for our cluster calculations has been described several times [12–15].

In Ref. [11] it has been shown that the adsorption of CO on a Pt(111) surface leads to a convergence with already 15 to 20 Pt-atoms. But this statement is not valid for many other systems.

The full quantum-mechanical treatment of systems with more than 30 atoms is (almost) impossible in practise. For example, the calculation of one point of the potential energy curve for the Al-Al₇₃ system needs between one and two weeks on a normal workstation. Therefore it was necessary to develop new approximations that permit the simulation of large systems.

We divide the whole system in a cluster part (*cl*) and the environment (*env*) and therefore the density, that is the important ingredient of the density functional method, can according to [5] also be divided in two different parts. In our case we use an expansion in atomic radial densities (expanded in higher multipoles) to divide the density into two parts

$$\tilde{\varrho}(\mathbf{r}) = \tilde{\varrho}^{cl}(\mathbf{r}) + \tilde{\varrho}^{env}(\mathbf{r}). \quad (1)$$

$\tilde{\varrho}$ is the approximative density created by the atomic radial densities. Because the cluster part is calculated self-consistently we can replace $\tilde{\varrho}^{cl}$ by the SCF-density ϱ^{cl} . We assume that the inner cluster is large enough so that the influence of the adsorbate on the environment can be neglected. Then the action of the environment onto the cluster can be treated as an external potential due to the external charge density $\tilde{\varrho}^{env}(\mathbf{r})$. This external potential consists of three parts

$$V^{ext}(\mathbf{r}) = V_{ext(\mathbf{r})}^N + V_{ext}^C(\mathbf{r}) + V_{ext}^{xc}(\mathbf{r}). \quad (2)$$

These three parts are the external Coulomb potentials of the nuclei and the electrons and the exchange-correlation potential. The exchange-correlation potential with different functionals [16–19] is in general given by

$$V_{ext}^{xc}(\mathbf{r}) = V^{xc}(\varrho^{cl} + \tilde{\varrho}^{env}) - V^{xc}(\varrho^{cl}) - V^{xc}(\tilde{\varrho}^{env}). \quad (3)$$

For a neutral environment the nuclear and the electronic Coulomb potential compensate each other at large distances. Therefore the effective Coulomb potential originates only from a region near the interface between cluster and environment. The same fact holds true for the exchange-correlation potential V_{ext}^{xc} (3), because it is only non-zero in the overlap region of ϱ^{cl} and $\tilde{\varrho}^{env}$.

The Kohn-Sham-equation [20] with the external potential reads:

$$(\hat{t} + V_{cl}^N(\varrho^{cl}) + V_{cl}^C(\varrho^{cl}) + V_{cl}^{xc}(\varrho^{cl}) + V^{ext}) \psi_i = \varepsilon_i \psi_i. \quad (4)$$

This equation is solved self-consistently with respect to $\varrho^{cl} = \sum_{i=1}^M n_i \psi_i^+ \psi_i$, where i runs over all occupied cluster electrons.

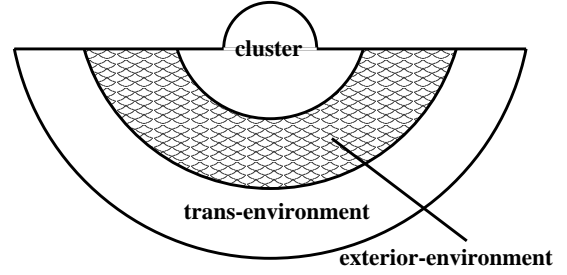


Fig. 1. The system is divided in three parts that are handled differently: cluster, transition-environment and exterior-environment.

Using the solution of the KS-equations (4) the total energy can be written

$$E^{tot} = \sum_{i=1}^M n_i \varepsilon_i - \frac{1}{2} \int V^C \varrho^{cl} d^3r - \int V^{xc} \varrho^{cl} d^3r + E^{xc} + \frac{1}{2} \sum_{K=1}^N \sum_{K' \neq K}^N \frac{Z_{K'} Z_K}{|\mathbf{R}_{K'} - \mathbf{R}_K|}. \quad (5)$$

Compared to the expression of a free cluster the influence of the environment is absorbed in the energy eigenvalues ε_i and the eigenfunctions ψ_i and therefore the density ϱ^{cl} .

As a first assumption for the external density distribution $\tilde{\varrho}^{env}$ we used a superposition of free atomic densities located at the sites of the environmental atoms (in part 3 this is called *neutral*). A better approximation is the usage of realistic atomic densities of a solid (later *SCF*). Comparing to a homogeneous solid in a real surface the atomic charge densities vary with the distance to the surface. Therefore we calculated the whole system (cluster+environment) without adsorbate self-consistently and used the charges at the environmental sites as sources for the external potential (2).

One technical problem for the implementation of this embedding approach was the treatment of the region near the interface between cluster and environment. The cluster wavefunctions still have tailed that reaches into the environmental region. Therefore the normal integration scheme of the cluster-code had to be improved in this region, that we call *transition-environment* (Fig. 1).

3 Results and discussion

3.1 Cluster expansion without environment

To test the embedding scheme we calculated the adsorption energy and distance of an Al ad-atom on the four-fold site of an Al(100) surface as a first example. For the Al atoms we used a basis set of $1s-3p_{3/2}$ wave-functions that were optimized with respect to the total energy of the dimer Al₂. Because of the large size of the cluster and environment it was not possible to take additional wave-functions into account. Moreover, the calculations with small clusters showed that these additional functions become less important when larger clusters are used. First

Table 1. Calculations for two different xc-functionals without any environment. To compare the values with the other groups [21–23] one has to take the rLDA-results.

| System | Adsorp. energy [eV] | | Bond distance [a.u.] |
|-------------------------|---------------------|---------|----------------------|
| | rLDA | B88/P86 | |
| Al–Al _{4.0.0} | –1.9 | –1.3 | 3.7 |
| Al–Al _{16.0.0} | –2.8 | –2.3 | 4.0 |
| Al–Al _{4.5.0} | –2.7 | –2.1 | 3.4 |
| Al–Al _{12.5.0} | –2.9 | –2.1 | 3.2 |
| Al–Al _{12.5.4} | –2.4 | –1.7 | 3.1 |
| Kürpick [23] | –2.90 | | 3.21 |
| Feibelman [22] | –2.93 | | 3.25 |
| Stumpf, Scheffler [21] | –3.77 | | 3.21 |

we tested the convergence of the characteristic physical quantities the adsorption energy and adsorption distance to the surface without any cluster-embedding. The results of these calculations are shown in Table 1.

We started with the system Al–Al_{4.0.0} (this means Al adsorbs at an Al-cluster with 4 atoms in the first layer and 0 atoms in the second and third layers) and increased the system in lateral as well as in vertical direction. We calculated the potential energy curves for the following systems: Al–Al_{16.0.0}, Al–Al_{4.5.0}, Al–Al_{12.5.0}, Al–Al_{12.5.4}. For all systems the Al–Al bond distance was set to the bulk value of 2.863 Å.

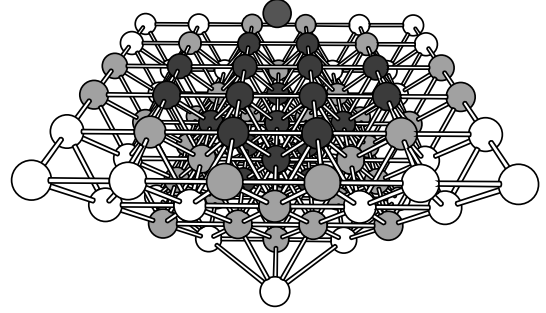
Comparing the calculated values one can see that the lateral expansion causes an increase in adsorption energy. But for the larger system Al–Al_{12.5.0} the vertical expansion shows the opposite effect. To give an explanation for this effect one has to take into account that the additional borders (that a cluster has compared to a surface) changes the charge densities of the outermost atoms directly and therefore the charge densities of the inner atoms (near the adsorption site) indirectly.

For the bond distances the behaviour is different. Increasing the system changes the value for the bond distance only little if the system is larger than Al–Al_{4.5.0}. Comparing the results for the bond distances to those of the other groups it seems that a two-layer cluster with about 9 atoms is enough to get a good description.

Summarizing these calculations we get a good agreement in adsorption distance for systems larger than Al–Al_{4.5.0}. But there was no convergence in adsorption energy with our cluster sizes. This is in correspondence to Stumpf and Scheffler [21] who needed about 500 atoms to get convergence. But comparing the energies for the calculated systems whose numbers of atoms are similar to those that Feibelman [22] and Kürpick [23] used there is an agreement.

3.2 Embedded cluster expansion

The results of the calculations without environment showed that the expansion of the cluster changed the ad-

**Fig. 2.** Model of the embedded system Al–Al_{12.5.4}. The darkest particles of the surface and the adsorbate form the cluster. The middle-dark particles are the transition-environment and the white atoms are the exterior environment.**Table 2.** Calculations for the embedded systems (energies only in rLDA-approximation).

| System | Env. occ. | Adsorp. energy [eV] | Bond distance |
|-------------------------|-----------|---------------------|---------------|
| | | rLDA | [a.u.] |
| Al–Al _{4.0.0} | neutral | –2.0 | >11 |
| Al–Al _{4.0.0} | SCF | –1.5 | 8.2 |
| Al–Al _{4.5.0} | neutral | –3.3 | 3.3 |
| Al–Al _{4.5.0} | SCF | –3.9 | 3.4 |
| Al–Al _{12.5.4} | neutral | –3.6 | 3.2 |
| Al–Al _{12.5.4} | SCF | –4.0 | 3.3 |
| Kürpick [23] | | –2.90 | 3.21 |
| Feibelman [22] | | –2.93 | 3.25 |
| Stumpf, Scheffler [21] | | –3.77 | 3.21 |

sorption energy but a convergence could not be achieved. Therefore, full quantum-mechanically inner clusters of different size were embedded into the surrounding environment as shown in Fig. 1. A transition environment of one atomic layer surrounding the cluster was used. The remaining atoms (about 130) were used for the exterior environment. Again the internuclear distances were kept fixed to the bulk value.

As explained before the embedding calculations were performed with two different choices for the environmental occupation. First, the adsorption was studied straightforwardly by putting the densities of neutral Al-atoms at the positions of the environmental atoms. For the inner clusters we have chosen an Al_{4.0.0}, Al_{4.5.0} and Al_{12.5.4} (Fig. 2) cluster. The results of the calculations are summarized in Table 2 (neutral).

If the inner cluster consists of only 4 atoms in the first layer the bond distance of the ad-atom with more than 11 a.u. is far off any reasonable value, indicating, that the cluster size is obviously too small. If a second layer is taken into account (Al_{4.5.0}), the situation is drastically improved. An adsorption energy of 3.3 eV and an adsorption distance of 3.3 a.u. is obtained. A further improvement is achieved by enlarging the cluster to Al_{12.5.4}. In particular, the adsorption distance exhibits a good convergence and is in good agreement with other theoretical values.

After that we discuss the influence of modified environmental occupation numbers for the generation of the embedding potential. These occupation numbers were obtained by a full self-consistent large cluster calculation of a 73 atomic cluster without the adsorbate. In contrast to the occupation numbers of neutral environmental atoms used before one gets slight variations in the occupations of the cluster and the environmental atoms and thus another environmental embedding potential. With this SCF-environment we recalculated the three systems. Even with this modification it can be seen from Table 2 (SCF) that an embedding of an $\text{Al}_{4,0,0}$ cluster is still not sufficient. On the other hand, using the modified embedding potential for the other two clusters ($\text{Al}_{4,5,0}$ and $\text{Al}_{12,5,4}$), a change in adsorption distance of about 0.1 a.u. and in the adsorption energy of 0.6 eV and 0.4 eV, respectively, is obtained.

Comparing the results of the embedded cluster calculations with those without environment only minor changes in the adsorption distance of the ad-atom are observed: For the $\text{Al}_{12,5,4}$ cluster without environment we get 3.1 a.u. while with the neutral environment 3.2 a.u. The same behaviour can be observed for the $\text{Al}_{4,5,0}$ cluster. On the other hand, an embedded calculation leads to more significant changes in the adsorption energies. For a neutral environment occupation we get an adsorption energy of 3.3 eV and an adsorption distance of 3.3 Å. The distance is in a suitable agreement with Stumpf and Scheffler's calculations, but there is a difference of 0.5 eV in energy. But using the SCF-environment we get a better agreement. For the largest embedded system ($\text{Al-Al}_{12,5,4}$) the adsorption energy varies only little and the energy differs only 0.2–0.3 eV around the value of Stumpf and Scheffler.

Surprising was the increase of 0.8 eV in adsorption energy if the systems were embedded. It seems that only the additional effects caused by the environment make the results comparable to those of Stumpf and Scheffler who took large enough clusters so that they calculated with converged cluster-sizes.

4 Conclusion

In this article a cluster embedding method was presented and applied to the adsorption of a single ad-atom on an $\text{Al}(100)$ surface. Although we have focussed our development on the low- Z element aluminium where relativistic effects do not play such an important role for the chemical bonding of the cluster, we conclude that the embedding scheme works and gives reliable results. The aim here was to make a first step towards a fully relativistic quantum mechanical description of adsorption processes.

The results for the clusters without environment shows that there is only little change in adsorption distance for systems larger than $\text{Al-Al}_{4,5,0}$. But for adsorption energy the expansions in lateral and vertical directions have opposite effects. Compared to the values which Feibelman and Kürpick have calculated there is a good agreement. One reason for this may be due to the same cluster size of about 20 atoms.

Because the convergence was not achieved with the cluster expansion without environment, we embedded the cluster into two different environment types. There we see that we get suitable results even with the embedded system $\text{Al-Al}_{4,5,0}$. If we use the SCF-environment for this system the results are in good agreement with those of Stumpf and Scheffler. For the largest system $\text{Al-Al}_{12,5,4}$ this is valid for both environment types. To sum up it can be said that the embedding procedure proposed here is a first step to describe bulk of surface effects in real space full relativistically.

To improve this approach it is necessary to calculate an external potential for the environment that fits best to an unlimited surface. To get the corresponding occupation numbers we plan to develop a copy-procedure. In it a cluster with environment will be calculated self-consistently. After each SCF-iteration the calculated occupation numbers of the inner cluster are transferred to the corresponding atoms of the environment. After convergence we get occupation numbers for the environment that will represent a surface.

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