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Adsorption of super-heavy elements on metal surfaces

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Abstract. The theoretical description of the adsorption of atoms on surfaces is still a big problem especially when the atoms involved are very heavy such that relativistic effects play an important role. During the last years we have developed a relativistic molecular program [1] which solves the relativistic Kohn-Sham equations with the use of various density functionals. We discuss here the adsorption of heavy elements on a Au(100) surface. The surface is simulated by different clusters in order to check at which position the ad-atom is adsorbed. Our main task here is to calculate the difference in the adsorption energies between the super-heavy element 112 and its homologue Hg.

PACS. 31.15.Ew Density-functional theory

1 Introduction

First detection of the element 112 was made a few years ago by the GSI laboratory, Darmstadt, but the study of its chemical properties is still a big challenge. Due to the short half-lives in the region of the super-heavy elements one important method to study their chemical behaviour is the use of gas-phase chromatography techniques. It is expected that only a few events can be detected so that one should know the adsorption energy which determines the adsorption. Of special interest is the difference between this quantity for element Hg and its homologue element 112. Up to now there are only a few theoretical predictions of the physical and chemical properties of this element [2].

From the very first atomic calculations of the super-heavy elements [2] it became clear that element 112 is the homologue of Hg as it is also expected from the trivial continuation of the periodic table. The main difference to Hg is that the two outer $7s^2$ shell electrons in element 112 are even more bound than the $6s^2$ electrons in Hg, and the spin-orbit splitting of the full $6d$ shell is much bigger than the $5d$ shell in Hg. Pershina *et al.* [3] calculated already the electronic structure of the dimers HgX and 112X (with X = Pd, Ag, Au), using the fully relativistic density-functional method with the relativistic general gradient approximation (GGA) for the exchange-correlation potential. Their calculation shows an increase in the bond length R_e and a decrease in the binding energies D_e from HgX to 112X, which is explained by the very strong relativistic stabilisation of the $7s^2$ shell.

In order to make a prediction of the adsorption enthalpy of element 112 on a Au(100) surface we present in this paper calculations of this quantity and compare them with the analogue ones for Hg.

2 Method

We describe a molecular system using the Density Functional Method. According to this method the total energy is given by the expression (we use atomic units):

$$E = \sum_{i=1}^{M} \langle \psi_i \mid \hat{t} \mid \psi_i \rangle + \int V^N \varrho \, \mathrm{d}^3\boldsymbol{r} + \frac{1}{2}\int V^C \varrho \, \mathrm{d}^3\boldsymbol{r} + E^{xc} + \frac{1}{2}\sum_{p,q} \frac{Z_p Z_q}{|\boldsymbol{R}_p - \boldsymbol{R}_q|} \quad (1)$$

with the electronic density

$$\varrho(\boldsymbol{r}) = \sum_{i=1}^{M} n_i \psi_i^{+}(\boldsymbol{r}) \psi_i(\boldsymbol{r}).$$

The index i runs over all occupied molecular orbitals M, which are four-component Dirac-spinors.

The Dirac kinetic energy operator has the form

$$\hat{t} = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + c^2(\beta - 1).$$

V^N is the nuclear potential

$$V^N(\boldsymbol{r}) = \sum_p \frac{Z_p}{|\boldsymbol{R}_p - \boldsymbol{r}|}$$

and V^C is the electronic Coulomb potential

$$V^C(\boldsymbol{r}) = \int \frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \mathrm{d}^3\boldsymbol{r}'.$$

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E^{xc} is the exchange-correlation functional.

The variation of the energy functional (1) leads to the relativistic Kohn–Sham equations [4]:

$$\left(\hat{t} + V^N(\boldsymbol{r}) + V^C\left[\varrho(\boldsymbol{r})\right] + V^{xc}\left[\varrho(\boldsymbol{r})\right]\right)\psi_i(\boldsymbol{r}) = \varepsilon_i \psi_i(\boldsymbol{r}) \tag{2}$$

where the exchange-correlation potentials is:

$$V^{xc}(\boldsymbol{r}) = \frac{\delta E^{xc}(\varrho)}{\delta \varrho(\boldsymbol{r})}\cdot$$

For the self-consistent solution of the equations we use the relativistic local density approximation [5,6] with the Vosko, Wilk and Nusair parameterization [7] for correlation. Nonlocal corrections are used perturbatively for exchange (with the relativistic form RGGA of Becke's [8] approximation) and correlation (Perdew functional) [9].

To solve the Kohn-Sham equations (2) we use the Molecular-Orbital Linear Combination of Atomic Orbitals (MO-LCAO)-method. This leads to the secular equation:

$$\underline{\underline{H}}\,\underline{c} = \underline{\underline{S}}\,\underline{c}\,\underline{\underline{\varepsilon}}$$

where $\underline{\underline{H}}$ and $\underline{\underline{S}}$ are the Fock and overlap matrices respectively, $\underline{c}$ is the coefficient-matrix and $\underline{\underline{\varepsilon}}$ is the eigenvalue matrix.

We use in our method optimized basis sets obtained from dimer calculations using the same program. These are formed from two parts:

- a minimal basis set,
- and additional optimized atomic basis functions.

The procedure which we used for optimization is the following:

- in the first step the total energy curve with the minimal basis set is calculated;
- at the internuclear separation which corresponds to the minimum of the total energy the wave functions which describe the valence electrons are slightly ionized; we optimized these valence wave functions (5*d* and 6*s* for Au and Hg, respectively 6*d* and 7*s* for 112) until we found the minimum of the total energy as a function of the degree of ionization;
- we add successively basis functions of the next few unoccupied orbitals from ionized atoms; again, the optimization is made for the total energy as a function of the degree of m ionization.

Our optimized basis includes the additional functions 6*p* and 5*f* for Au and Hg, and 7*p* and 6*f* for 112.

In order to reduce the numerical effort for these heavy elements we used the frozen core approximation, because the inner orbitals do not change their form during the adsorption process so that they can be kept fixed in the self consistent procedure. This assumption has been tested by all-electron calculations.

3 Results and discussions

As a starting point which also is used to optimize the basis functions as explained in Section 2 we present the results for the dimers HgAu and 112Au in Table 1. We list the RLDA and GGA corrected results for the binding energies in eV as well as the RLDA bond distance in a.u. The values in Table 1 differ from the results presented in reference [3] by small amounts because our optimization included additional *nf* functions.

Table 1. Binding energy and bond distance (RLDA) for the HgAu and 112Au dimers.

System	Binding energy [eV]		Distance
	RLDA	GGA	[a.u.]
HgAu	–1.03	–0.55	4.9
112Au	–0.93	–0.41	5.0

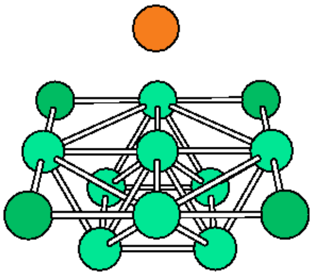

Fig. 1. Top position (the surface was simulated by 13 atoms).

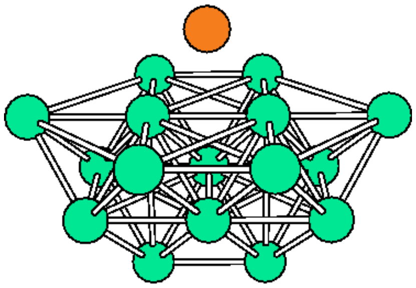

Fig. 2. Bridge position (the surface was simulated by 16 atoms).

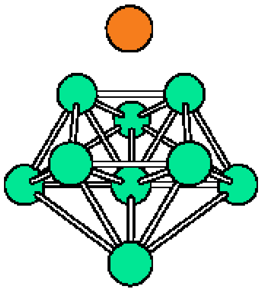

Fig. 3. Hollow position (the surface was simulated by 9 atoms).

In our calculations for the adsorption we approximate the surface by moderate clusters. Due to the fact that these calculations are very time-consuming we have to restrict to relatively small clusters which are shown in Figures 1 to 3 for the three possible positions of the adsorption of ad-atom on the surface.

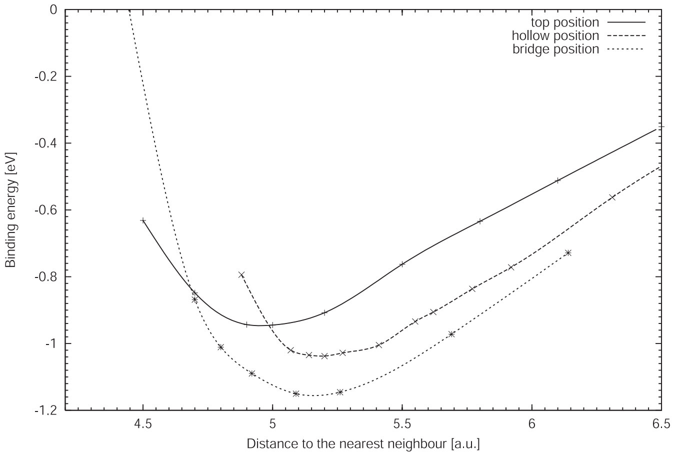

Fig. 4. The potential energy curves for the adsorption of Hg on the Au clusters.

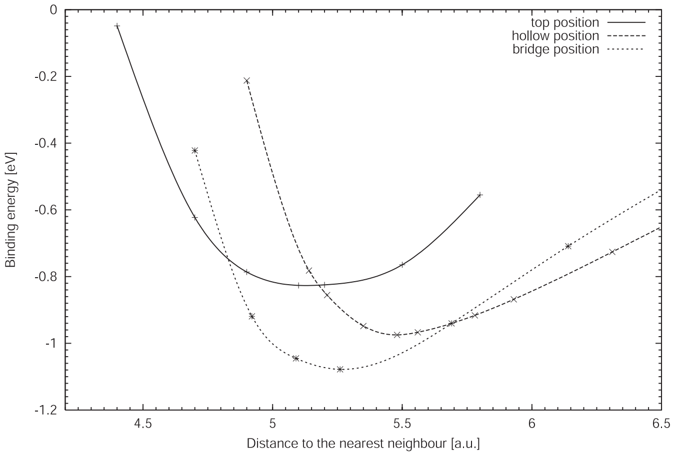

Fig. 5. The potential energy curves for the adsorption of element 112 on the Au clusters.

The distances between the atoms of the clusters are kept fixed to their bulk values. In the case of top and hollow position (Figs. 1 and 3) the C_{4v} symmetry was used and for the bridge position (Fig. 2) C_{2v}.

Figures 4 and 5 present the potential energy curves of Hg respectively 112 on these three clusters as function of the distance to the nearest neighbours in the RLDA approximation. The values which describe the minima are summarized in Tables 2 and 3. In both cases the binding energy of element Hg respectively 112 at the bridge position as shown in Figure 2 is the largest. Comparison between Hg and 112 shows that for all positions lead to a somewhat stronger binding for Hg of about 0.06 eV than for 112, for the bridge and hollow position, respectively with 0.11 eV for the top position. Comparison of these values shows that there is a stronger binding for Hg of about 0.06 eV compared with element 112 for hollow and bridge position. For the top position this value is 0.12 eV. As shown in Table 1 the difference for the dimer is 0.1 eV.

Table 2. Binding energy and bond distances of Hg on the Au clusters (RLDA).

System	Binding energy [eV]	Distance to the surface [a.u.]	Distance to the nearest neighbour [a.u.]
top	–0.94	5.0	5.0
bridge	–1.15	4.3	5.08
hollow	–1.04	3.5	5.2

The predicted value [10] of the binding energy: −1.01 eV.

Table 3. Binding energy and bond distances of element 112 on Au clusters (RLDA).

System	Binding energy [eV]	Distance to the surface [a.u.]	Distance to the nearest neighbour [a.u.]
top	–0.82	5.1	5.1
bridge	–1.08	4.5	5.3
hollow	–0.99	3.8	5.4

The distances to the nearest neighbour corresponding to the minima of the potential energy curves show a small increased from the top to the bridge and hollow position. This is consistent with our expectation, since in the top position the bounding is dominated by the interaction with the only one nearest cluster–atom. For the bridge position we have two and for the hollow position four nearest neighbours. After applying the GGA correction we come to a final value of −0.65 eV for the binding energy of Hg on Au and −0.56 eV for 112 on Au. Rossbach *et al.* [10] give a value for the adsorption energy of Hg on Au of 1.01 eV so that our extrapolation for 112 on a Au surface is in the order of 0.9 ± 0.05 eV.

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