The study of adsorption of hydrogen onto copper and gold clusters by method of the density functional

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Abstract. The paper presents the results of quantum-chemical modeling of gold and copper nanoparticles and a comparison of their adsorption properties with the example of interaction with hydrogen atoms. The goals of the work were both a fundamental study of the electronic structure and the elementary act of the heterogeneous catalysis reaction and the comparison of gold and copper nanoparticles as catalysts for the hydrogenation reaction.

1. Introduction
Bulk copper has good electrical conductivity (the best of any metal, except silver), thermal conductivity and plasticity, that determines its value in various areas of practical application. Nanostructured copper also has a high potential for use in catalysis, production of functional materials, medicine and energy. A wide range of applications is due to the high catalytic and chemical activity of copper-based nanostructures, which has been studied and demonstrated in a variety of works, both experimental [1-4], and theoretical [5-8]. In addition, it is important to note that the synthesis of copper nanoparticles is cheaper compared to gold and platinum nanoparticles. All this makes copper nanoparticles extremely attractive for use as catalysts for a variety of reactions. In the present work, the hydrogenation reaction, namely, the interaction of a nanocluster of copper with a hydrogen atom, is considered.

2. DFT-study and discussion
2.1. Calculation method
A numerical experiment is performed using the density functional theory. Software packages OpenMX3.8 и QuantumEspresso 5.1.1 are used for calculations. In both cases, the generalized gradient approximation and the PBE functional were chosen. The relativistic effects of the electrons motion were taken into account in the generation of pseudopotentials. The accuracy of the chosen basis sets roughly corresponded to the double Slater basis function. For the given purposes did not include achievement of experimental values, therefore in order to avoid ambiguities in calculations the overlapping of bases is not considered.

2.2. Cluster models
The models of gold and copper nanoparticles were Auₙ and Cuₙ (n = 13, 20, 55) clusters. The atomic structure of the clusters is calculated using quasi-Newtonian methods and corresponded to a local minimum of the total energy. The search for a global minimum was not the goal of the work. The
obtained stable isomers of clusters, even those with filled icosahedral shells, \( n = 13, 55 \), have no certain type of symmetry, and that agrees with previous studies [9]. As an example, 13-atoms isomers of gold and copper clusters are shown in figure 1. The symmetry of this clusters is close to icosahedral.

Calculations of binding energy between atoms in clusters have shown the expected dimensional effect: an increase in the binding energy takes place with an increase in the nuclear system, that is explained by a decrease in the fraction of surface atoms in larger clusters (table 1). It is worth pointing out that the binding energy in copper clusters is greater.

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\text{Table 1. The binding energy between gold atoms in clusters.}
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| Cluster | \( \text{Au}_{13} \) | \( \text{Au}_{20} \) | \( \text{Au}_{55} \) | \( \text{Cu}_{13} \) | \( \text{Cu}_{20} \) | \( \text{Cu}_{55} \) |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Binding energy, eV | –1.95 | –1.99 | –2.19 | –2.40 | –2.53 | 2.87 |

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\text{Figure 1. 13-atoms isomers of gold (left) and copper (right) clusters, used in the numerical experiment in this paper.}
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\text{Figure 2. Density of states (DOS) for clusters of gold and copper of various sizes, } n = 13, 20, 55.
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Electronic spectra of gold and copper clusters of various sizes are shown in figure 2. As can be seen, the distribution of the density of states for the cluster \( \text{Cu}_{13} \) and \( \text{Au}_{13} \) has separate local maxima,
which gradually merge with an increase in the cluster size of Cu$_{55}$ and Au$_{55}$, forming the structure similar to the zone in a solid body. In addition to this demonstration of the size effect, attention should also be paid to the general distribution of the density of states for gold and copper clusters, the main part of which is located below the Fermi level. In general, the features of calculated density of states are in accordance with the detailed results for gold clusters, carried out in [10].

Like most metal clusters, gold and copper clusters of the same size have many almost isoenergetic isomers [11]. In particular, planar isomers of Au$_{13}$ and Cu$_{13}$ clusters are found in this work. It should be noted that the planar isomer of gold is energetically more stable than the icosahedral one (0.25 eV) [12], while in the case of copper the icosahedral isomer is more stable (0.32 eV). The distance between the nearest atoms in the gold cluster is $\sim 2.75$ Å, in copper $\sim 2.36$ Å, and the planes are formed by practically regular triangles (figure 3).

![Figure 3. Planar clusters of Au$_{13}$ and Cu$_{13}$.](image)

2.3. The hydrogen atom position

Table 2 shows the binding energies and lengths of the Au$_{13}$ cluster with hydrogen in different positions relatively to the nearest gold atoms. According to the calculations, the values of the energy and length of the Au-H bond at different positions of the hydrogen atom above the surface of the gold cluster differed insignificantly and averaged as 3.67 eV and 1.77 Å, respectively. However, the bridge-position is the most favorable.

| Position  | atop  | bridge | hollow | average |
|-----------|------|--------|--------|---------|
| Binding energy, eV | –3.62 | –3.75  | –3.64  | 3.67    |
| Bond length, Å  | 1.6  | 1.8    | 1.9    | 1.77    |

Table 3. The binding energy and bond length of the Cu$_{13}$ cluster with the hydrogen atom at different positions relatively to the nearest copper atoms.

| Position  | atop  | bridge | hollow | average |
|-----------|------|--------|--------|---------|
| Binding energy, eV | –2.59 | –3.13  | –3.18  | 2.97    |
| Bond length, Å  | 1.5  | 1.65   | 1.7    | 1.62    |
Carrying out similar calculations for the copper cluster Cu_{13} has shown that hollow-position of the hydrogen atom on the cluster surface is the most stable (table 3). Differences in the magnitude of the binding energy between bridge- and hollow-positions are small. Hydrogen atom binding energy in the atop-position is much smaller. The average binding energy and bond length are 2.97 eV and 1.62 Å, respectively.

2.4. Locality

In order to establish how decidedly the interaction with hydrogen affects the electronic structure of gold and copper clusters, the distribution of the projected density of states on atoms with and without a hydrogen atom is calculated. The local electronic density of d-states on gold and copper atoms interacting with hydrogen decreases with the formation of a bond with hydrogen (figure 4 (a) and (c)). The changes in the distribution of the local density of states for a neighboring atom are much smaller (figure 4 (b) and (d)). Thus, sequential adsorption acts for clusters of gold and copper can be considered independent – in the sense of smallness of the spatial perturbation region determined by the adsorption, that is \( E(k) - E(k+1) \ll (E(k), E(k+1)) \), where \( E(k) \) is adsorption energy of the \( k \)-th hydrogen atom.

![Figure 4](image)

**Figure 4.** The projected density of states on the gold and copper atoms with a hydrogen atom (a) and (c), on the adjacent atom (b) and (d), in states without (PDOS1) and with (PDOS2) hydrogen.

2.5. Sequential adsorption of hydrogen atoms

Also, to estimate the effect of interaction with hydrogen atoms on the energy structure, the density of states for clusters Au_{13}, Au_{20}, Au_{55}, Cu_{13}, Cu_{20}, Cu_{55} is calculated without hydrogen atoms and with a surface completely filled with hydrogen atoms (figure 5). With an increase in the number of hydrogen atoms, the first moment of density of states distribution (d-band center) shifts from the Fermi level towards negative values of energy in case of gold and also copper clusters, which means a decrease in
the chemical activity of the cluster, according to the resonance model of chemisorption. The measure of the chemical activity in this case is the value of the binding energy.

Figure 5. Density of cluster states $\text{Au}_n\text{H}_m$, where $n = 13, 20, 55, 100, 147$, $m = 1–86$.

Table 4. The binding energy of hydrogen atoms with gold and copper clusters [13].

| $m$ | $\text{Au}_{13}$, eV | $\text{Au}_{20}$, eV | $\text{Au}_{55}$, eV | $\text{Cu}_{13}$, eV | $\text{Cu}_{20}$, eV | $\text{Cu}_{55}$, eV |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | $-3.13$         | $-3.22$         | $-3.50$         | $-3.29$         | $-3.35$         | $-3.15$         |
| ful | $-3.14$         | $-3.26$         | $-3.14$         | $-3.27$         | $-3.23$         | $-3.22$         |

The calculated values of the binding energy of hydrogen atoms in gold and copper clusters for various surface occupancies are shown in table 4: with only one hydrogen atom and with complete filling. A complete correlation with changes in the energy spectra of the clusters does not occur, that indicates the complication of the resonance model of chemisorption. This leads to conclusion that the value of the binding energy in the investigated objects is determined not only by the coordination
saturation of the copper and gold atoms, but also by the distribution of the local density of states near the Fermi level. Since the chosen clusters have low nuclearity, their chemical properties can be determined to a considerable extent not only by the local density of d-states below the Fermi level, but also by sp-states that are smaller in value but close to the Fermi level.

2.6. Delocalization

As it is known, clusters with highly symmetric geometric structure or clusters with a complete filling of a certain group of electronic states are distinguished by increased stability ("magic" clusters).

The electronic structure of gold ([Xe]4f145d106s1) and copper ([Ar]3d104s1) atoms allows to consider nanosystems based on these elements can exhibit features that correspond to both "geometric" (the main contribution to the interaction of atoms is made by d-electrons, similar to transition metals) and "electronic" (one "external" s-electron, as in alkali metals) magic numbers. The calculations did indeed show a nonlinear dependence of the binding energy of gold and copper clusters with hydrogen atoms for certain values of the total number of atoms \(n + m\) in clusters \(\text{Au}_n\text{H}_m\) and \(\text{Cu}_n\text{H}_m\) corresponding to the "electronic" series of magic numbers, namely in the vicinity of 18 and 20 (figure 6).

![Figure 6](image)

**Figure 6.** Dependence of the binding energy on the number of adsorbed hydrogen atoms in clusters \(\text{Au}_n\text{H}_m\) (a) and \(\text{Cu}_n\text{H}_m\) (b), where \(n = 13, m = 1–12\).

Deviations from the exact values of magic numbers arise due to the asymmetric structure of heterogeneous clusters. This means that the replacement of metal atoms by chemisorbed hydrogen atoms in the construction of the outer electron shell of the cluster is inherent both for gold and copper. At the same time, the electrons added by hydrogen are delocalized throughout the volume. However, the general redistribution of the electron density in the heterogeneous metal-hydrogen system is insignificant, that agrees with the previously drawn conclusion about the locality of the introduced perturbations. A similar effect – some kind of the electronic and atomic structure of silicium hydride with the replacement of hydrogen by gold – is detected and investigated by photoelectron spectroscopy in [14].

3. Conclusions

Acts of sequential adsorption in the studied systems can be considered as independent. As the number of adsorbed hydrogen atoms increases, the d-band center shifts toward smaller values of energy.

In the outer electron shell of a heterogeneous metal-hydrogen cluster, the electrons of chemisorbed hydrogen atoms play the same role as delocalized s-electrons of metal atoms.

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