SPIN-ORBIT COUPLING IN GOLD NANOSTRUCTURES

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Abstract. The effect of spin-orbit interaction accounting on the atomic and electronic structure of 0*D* (clusters), 1*D* (gold nanotubes), and 2*D* (monolayer) gold is reported. The relevance of the work lies in the fact that, on the one hand, gold nanostructures are widely used, in particular, in sensorics and medicine, on the other hand, due to limited computing resources, researchers may neglect some effects in the theoretical study of such objects, and it is important to understand what errors may be associated with such neglect. The study was conducted on a large set of objects: six isomers of the Au_{25} cluster, gold nanotubes of nine different radii, and a flat monolayer of gold, which made it possible to comprehensively evaluate the effect of spin-orbit interaction. It has been shown that the cohesive energies of all but the thinnest of the gold nanotubes range from the cohesive energy of gold nanoclusters to the cohesive energy of a gold monolayer. Accounting for the spin-orbit interaction leads to a decrease in the Au–Au interatomic distances and a change in the electronic structure of gold nanoobjects. At the same time, a significant change in the position of energy levels is possible for nanoclusters, reflecting a change in the cluster structure. For nanotubes and golden, only the splitting of energy levels occurs near the Fermi level.

Keywords: *golden, golden nanotube, Au_{25} cluster, DFT, band structure, spin-orbit interaction*

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INTRODUCTION

The interest of researchers in gold-based nanomaterials is associated with a wide range of possibilities for their practical use, a special place among which is occupied by sensorics and medical applications [1, 2]. Gold at the nanoscale can be structured in different ways: nanoclusters, nanowires [3], flat monolayer gold (golden) [4].

Gold clusters are used to enhance Raman spectra by surfaces [5], which allows them to be considered as sensors [6]. In addition to unstabilized gold clusters, their stabilized analogs have recently attracted much attention, being actively used, for example, in hydrogen evolution reactions [7] and oxygen reduction reactions [8]. The fact is that the atomic structure of gold clusters and their electronic structure [9] turn out to be significantly dependent on the chemical environment (the presence of stabilizing fragments) and there is no reason to believe that the properties of the clusters remain unchanged during stabilization. The properties of clusters also change when interacting with each other: the response of individual clusters to external influences can be enhanced due to the formation of superstructures [10].

Gold nanowires find application in wearable bioelectronics and as conductive channels [11]: nanowires allow for forming a better metal-polymer contact compared to gold foil due to the larger contact area [12]. Vertically oriented arrays of gold nanowires on substrates are used for highly sensitive detection of pathogens using surface-enhanced Raman spectroscopy [13]. The work [14] reports the fabrication of switches and strain gauges based on gold nanowires. Gold nanostructures are actively used together with carbon materials. Graphite electrodes modified with dendritic gold nanostructures can be used as glucose sensors [15]. Carbon nanotubes functionalized with gold nanothreads are used for the detection of bisphenol A [16]. Functionalized multi-walled carbon nanotubes decorated with gold nanoparticles can act as powerful antibacterial materials [17].

Gold, like several other elements [18, 19], can exist in the form of nanotubes [20, 21], which are a special case of nanowires. Recently, two-dimensional gold [4] was experimentally obtained, the possibility of which had been questionable for a long time. Due to the relatively weak bonds between gold atoms in nanotubes and goldene, they are not considered as reinforcing phases in composites, as is the case with carbon nanotubes [22, 23]. Thus, today it can be reliably stated that gold exists in zero-, one-, and two-dimensional states. In computer modeling of the properties of such objects, quantum-chemical programs implementing density functional theory are widely used.

Within the framework of density functional theory, vibrational spectra [24], electronic structure [25-27], electrical conductivity [25, 28] of single-walled gold nanotubes (SWGNTs), and adsorption of atoms on SWGNTs [27] and molecules on goldene [30] have been studied. The dependence of the electronic structure of SWGNTs on mechanical deformations [28, 31] has been investigated. In the work [32], it is shown that gold clusters of 24 atoms or more in some cases have a hollow framework structure similar to nanotubes.

For "heavy" elements, such as gold, relativistic corrections and spin-orbit interaction should be taken into account in DFT calculations. Accounting for spin-orbit interaction in isomers of the Au_{13} cluster increases the energy difference between planar and "bulk" isomers and leads to shorter bond lengths [33].

In work [34], when discussing the band structure of goldene, a strong spin-orbit interaction is mentioned, but it is not illustrated. In work [27], the possibility of accounting for spin-orbit interaction is mentioned, but there are no indications of its use for calculating the band structure of goldene. Meanwhile, the band spectra of goldene presented in works [34] and [27] differ significantly. Unfortunately, different modeling tools were used in the mentioned works, and it is impossible to attribute the observed differences to the influence of spin-orbit interaction.

Previously, we conducted studies of gold nanotubes both within the framework of density functional theory [35, 36] and by analytically solving the equations of the Hubbard model [37]. The purpose of this work is to determine the influence of spin-orbit interaction on the electronic structure of gold with reduced dimensionality: clusters, nanotubes, and a flat gold monolayer.

MODELS AND METHOD

The objects of modeling were clusters of 25 gold atoms $Au_{25,\,m}$, where m = 1-6, gold nanotubes with mirror symmetry (n, 0), where n = 3-10, and two-dimensional gold - goldene. Figure 1 shows their atomic structures. As starting configurations for clusters, we considered five structures of the Au_{25} cluster from work [30] (m = 1-5) and the gold base of a stabilized cluster [7] (m = 6).

Fig. 1. Models of (a) $Au_{25,m}$ clusters, where m = 1-6, (b) GNTs with chirality indices (n, 0), n = 3-10, and (c) goldene.

The modeling was performed using the density functional theory method implemented in the VASP program [38], which uses a plane wave basis. The energy cutoff for the plane wave basis was chosen to be 600 eV. PAW pseudopotential and PBE exchange-correlation functional were used.

The VASP program assumes periodic boundary conditions. For the case of clusters, the size of the simple cubic computational cell was 2.5×2.5×2.5 nm. The computational cell for nanotube modeling was chosen as rectangular with a translation parameter of 2.5 nm in directions perpendicular to the nanotube axis.

The computational cell for golden was hexagonal with a translation parameter of 2.5 nm in the direction perpendicular to the golden plane. Translation parameters not specified above were determined for each model independently from the condition of minimum total energy.

When dividing the reciprocal space according to the Monkhorst-Pack scheme for the above directions with a translation parameter of 2.5 nm, one k -point was taken for each. In the direction of the nanotube axis, 61 k -points were taken. For golden, the grid in reciprocal space was set by dividing 51×51×1 points.

The initial atomic structures of gold nanotubes and golden, illustrations of all models were obtained using the GUI4dft program [39]. The sumo program [40] was used to construct the band structure.

RESULTS AND DISCUSSION

Since the gold atom clusters considered in this work consist of the same number of atoms, their relative energy attractiveness can be evaluated by the total energy. The calculated relative total energies of Au_{25} isomers are shown in Fig. 2. From the figure, it can be seen that despite the significant difference in the modeling approach we used, the relative energies of the isomers $Au_{25,1}$, $Au_{25,2}$ and $Au_{25,4}$ agree quantitatively. For the isomers $Au_{25,3}$ and $Au_{25,5}$, the difference is 40%. This can be explained by the fact that the energy of isomers $Au_{25,1}$, $Au_{25,2}$, $Au_{25,4}$ decreases by approximately the same amount during structure optimization without symmetry constraints, while for isomers $Au_{25,3}$ and $Au_{25,5}$, no significant energy changes are observed during structure optimization. The relative energies of isomers $Au_{25,m}$ for m = 1-5 are several times lower than the corresponding value calculated for the cluster $Au_{25,6}$. This means that the structure obtained by optimizing the "core" of the ligand-stabilized gold cluster is indeed energetically unfavorable. It is metastable, since no transition to any other isomer occurs during the optimization process.

Fig. 2. Average interatomic distances $l_{\text{Au-Au}}$ and relative energies ΔE of Au_{25} isomers. The index "soc" refers to results obtained taking into account spin-orbit coupling. ΔE_{ref} - relative energies of the corresponding starting configurations of clusters according to [32].

Average interatomic distances (among those not exceeding 3 Å) for most Au_{25} isomers decrease when spin-orbit coupling is taken into account, but by no more than 0.6% (Fig. 2). The equilibrium translation period of nanotubes and golden changes by less than 0.4%. Similar behavior of interatomic distances is also observed in Au_{13} isomers [33]. Note, however, that the increase in the average interatomic distance for the $Au_{25,6}$ isomer does not mean bond elongation, but an increase in their number due to more atom pairs falling within the analyzed distance range. Moreover, for three of the six isomers ($m = 3, 5, 6$), spin-orbit coupling led to a decrease in the diversity of bond lengths, which can be attributed to an increase in the degree of structural symmetry.

To assess the energy stability of each model, cohesion energy E_{coh} and formation energy E_{form} were calculated:

$$E_{\text{coh}} = \frac{nE_{\text{at}} - E_{\text{model}}}{n},$$

$$E_{\text{form}} = \frac{E_{\text{model}} - n\mu}{n},$$

where E_{model} is the energy of the calculation cell, n is the number of atoms in the calculation cell, E_{at} is the energy of one isolated gold atom, μ is the chemical potential, assumed to be equal to the energy of one atom in an FCC gold crystal. The calculated cohesion and formation energies taking into account spin-orbit interaction are given in Table 1. Figure 3 shows a comparison of formation energies obtained with and without considering spin-orbit interaction.

Fig. 3. Cohesion and formation energies of gold nanotubes as a function of their radius.

Table 1. Cohesion energies E_{coh} and formation energies E_{form} of gold nano-objects

Object	E_{coh}, eV	E_{form}, eV
Au $_{25,1}$	2.47	0.70
Au25_2	2.46	0.71
Au25_3	2.45	0.71
Au25_4	2.46	0.71
Au25_5	2.45	0.72
Au25_6	2.37	0.80
AGNT (3, 0)	2.38	0.79
AGNT (4, 0)	2.50	0.66
AGNT (5, 0)	2.63	0.53
AGNT (6, 0)	2.72	0.45
AGNT (7, 0)	2.72	0.45
AGNT (8, 0)	2.78	0.38
AGNT (9, 0)	2.80	0.37
AGNT (10, 0)	2.80	0.36
golden	2.89	0.28

From Table 1, it can be seen that all obtained cohesion energies are less than the cohesion energy of FCC gold, which is 3.20 eV [32]. Among the gold nanoparticles we studied, the golden has the maximum cohesion energy, which can be represented as a gold nanotube with an infinitely large radius. Despite the fact that the study considers nanotubes of relatively small radius (up to 4.4 Å), the cohesion energy of the thickest nanotube is only 3% less than the cohesion energy of the golden. The cohesion energies of Au_{25} isomers are comparable to the cohesion energy of the thinnest nanotubes we considered.

When accounting for spin-orbit interaction, the cohesion energy for all gold nanoparticles considered in this work increases by approximately 0.1 eV. For gold nanotubes, this is shown in

Fig. 3. Similar reasoning could be presented based on the analysis of the formation energy of the gold nano-objects we considered.

In work [33], it is reported that spin-orbit interaction significantly affects the HOMO-LUMO gap magnitude of Au $_{13}$ cluster isomers. As can be seen from Fig. 4, the width of the HOMO-LUMO gap changes when spin-orbit interaction is taken into account in Au $_{25}$ isomers as well, but this occurs not so much due to level splitting as due to changes in level positions during additional structure optimization.

Fig. 4. Energy levels of Au$_{25}$ clusters with (red lines) and without (blue lines) spin-orbit interaction. Energy is measured from the HOMO.

Gold nanotubes have a metallic type of electrical conductivity [28, 35, 36]. The 5*d* - and 6*s* -electrons contribute to the density of states at the Fermi level. Most of the 5 *d* -states lie below the Fermi level, so despite the fact that there are 10 electrons at the 5 *d* -level and only one at the 6s level, the contribution of 5*d* -electrons only for a few investigated nanotubes (GONT (3, 0) and GONT (5, 0)) was several times greater than the contribution from 6 *s* -electrons. For most GONTs, the contribution of 6*s* -electrons to the density of states at the Fermi level is predominant. For platinum nanotubes, spin-orbit interaction leads to splitting of dispersion curves up to 0.5 eV [41]. We observe a similar effect for gold nanotubes (Fig. 5), but the magnitude of splitting is smaller. For golden, splitting of 0.5 eV can only be discussed for states that are more than 1 eV away from the Fermi level (Fig. 6), and the greatest influence is on states in the valence band.

Fig. 5. Band structure of gold nanotubes (*n*, 0), where *n* = 3–10. Red lines – with spin-orbit interaction, blue lines – without it.

Fig. 6. Band structure of golden without (blue dashed lines) and with (red lines) spin-orbit interaction.

CONCLUSIONS

This work demonstrates the range of possible changes in structural and electronic properties of gold clusters, nanotubes, and two-dimensional gold monolayer depending on whether spin-orbit interaction is considered or not in modeling using the generalized gradient approximation of density functional theory.

It is shown that accounting for spin-orbit interaction can lead to noticeable changes in the electronic structure of nanoclusters near the HOMO level, while for nanotubes and flat gold monolayer, such influence near the Fermi level is significantly weaker. This circumstance is explained by the fact that besides the reduction of average interatomic Au-Au distances in all gold nano-objects due to spin-orbit interaction, clusters can also experience changes in the "degree of symmetry" of the system.

Gold nanoclusters possess minimal cohesion energy. This means that one-dimensional and two-dimensional gold nanostructures are more stable: greater energy is required to separate them into non-interacting atoms. Along with the expected result that the formation energies of all considered nanoparticles are positive compared to FCC gold, it was shown that formation energies decrease with increasing radius of gold nanotubes, with the flat gold monolayer representing the limiting case.

CONFLICT OF INTERESTS

The authors of this work declare that they have no conflict of interest.

REFERENCES

1. *Liu X., Wei L., Wang X., He S., Yan Y., Li Q., H., Hu C., Ling Y.* Flexible strain sensors based on gold nanowire dominoes for human motion detection // Mater. Today Commun. 2023. V. 35. P. 105703.
2. *Zhou F., Shu L., Yimei T., Li W., Hai L., Zhang X., Li Y., Gao F.* Wearable electrochemical glucose sensor of high flexibility and sensitivity using novel mushroom-like gold nanowires decorated bendable stainless steel wire sieve // Anal. Chim. Acta. 2024. V. 1288. P. 342148.
3. *Hassan H., Sharma P., Hasan M.R., Singh S., Thakur D., Narang J.* Gold nanomaterials – The golden approach from synthesis to applications // Mater. Sci. Energy Technol. 2022. V. 5. P. 375–390.
4. *Kashiwaya S., Shi Y., Lu J., Sangiovanni D.G., Greczynski G., Magnuson M., Andersson M., Rosen J., Hultman L.* Synthesis of goldene comprising single-atom layer gold // Nature Synthesis. 2024. V. 3. № 6. P. 744–751.
5. *Al-Otaibi J.S., Mary Y.S., Mary, Y.S., Acharjee N., Al-Saadi A.A., Gamberini M.C.* Influence of pyramidal M_{20} (M = Cu, Ag and Au) clusters on SERS and noncovalent interactions toward tuberculosis drug pretomanid (PTD): DFT study // J. Comput. Biophys. Chem. 2024. V. 23. № 1. P. 47–61.
6. *Al-Otaibi J.S., Mary Y.S., Mary Y.S., Al-Saadi A.A.* Revealing the adsorption nature of disulfiram on metal clusters (Au, Pt, Ag, Pd, Cu, and Ni): DFT analysis, SERS enhancement and sensor properties // Comput. Theor. Chem. 2024. V. 1235. P. 114543.
7. *López-Estrada O., Mammen N., Laverdure L., Melander M.M., Häkkinen H., Honkala K.* Computational criteria for hydrogen evolution activity on ligand-protected Au_{25}-based nanoclusters // ACS Catal. 2023. V. 13. P. 8997–9006.
8. *Sun Z., Wang J., Su L., Gu Z., Wu X.P., Chen W., Ma W.* Dynamic evolution and reversibility of a single Au_{25} nanocluster for the oxygen reduction reaction // J. Am. Chem. Soc. 2024. V. 146. P. 20059–20068.
9. *Katsiev K., Lozova N., Wang L., Sai Krishna K., Li R., Mei W.N., Skrabalak S.E., Kumar C.S.S.R., Losovyj Y.* The electronic structure of Au_{25} clusters: Between discrete and continuous // Nanoscale. 2016. V. 8. P. 14711–14715.
10. *Kim S., Kim H., Lee C., Park I., Kim Y., Moon D., Shim J.H., Ryu S., Park S.S.* Au_{25} cluster-based atomically precise coordination frameworks and emission engineering through lattice symmetry // ACS Nano. 2024. V. 18. P. 29036–29044.
11. *Zhang H., Lin F., Cheng W., Chen Y., Gu N.* Hierarchically oriented jellyfish-like gold nanowires film for elastronics // Adv. Funct. Mater. 2023. V. 33. P. 2209760.
12. *Ikeda T.* Gold nanowire mesh electrode for electromechanical device // Sci. Rep. 2023. V. 13. P. 16669.
13. *Li K., Yang Y., Xu C., Ye Y., Huang L., Sun L., Cai Y., Zhou W., Ge Y., Li Y., Zhang Q., Wang Y., Liu X.* Vertical gold nanowires-based surface-enhanced Raman scattering for direct detection of ocular bacteria // Sensors Actuators B Chem. 2023. V. 380. P. 133381.
14. *Kim T.Y., Hong S.H., Jeong S.H., Bae H., Cheong S., Choi H., Hahn S.K.* Multifunctional intelligent wearable devices using logical circuits of monolithic gold nanowires // Adv. Mater. 2023. V. 35. P. 2303401.

15. *German N., Popov A., Ramanavicius A., Ramanaviciene A.* Development and practical application of glucose biosensor based on dendritic gold nanostructures modified by conducting polymers // Biosensors. 2022. V. 12. P. 641.
16. *Chang F., Ren K., Li S., Chang F., Ren K., Li S., Su Q., Peng J., Tan J.* A voltammetric sensor for bisphenol A using gold nanochains and carbon nanotubes // Ecotoxicol. Environ. Saf. 2023. V. 252. P. 114588.
17. *Ahmed D.S., Mohammed M.K.A.* Studying the bactericidal ability and biocompatibility of gold and gold oxide nanoparticles decorating on multi-wall carbon nanotubes // Chem. Pap. Springer International Publishing. 2020. V. 74. P. 4033–4046.
18. *Tomilina O.A., Konshyna A.A., Milyukovaa E.T., Tomilin S.V., Berzhansky V.N.* Correlation of the size factors of nanocatalyzer and carbon nanotubes // Phys. Met. Metallogr. 2022. V. 123. № 11. P. 1112–1116.
19. *Kozlovskiy A.L., Shlimasa D.I., Shumskayac A.E., Kaniukov E.Y., Zdorovets M.V., Kadyrzhanov K.K.* Influence of electrodeposition parameters on structural and morphological features of Ni nanotubes // Phys. Met. Metallogr. 2017. V. 118. № 2. P. 164–169.
20. *Oshima Y., Onga, A. Takayanagi K.* Helical gold nanotube synthesized at 150 K // Phys. Rev. Lett. 2003. V. 91. P. 205503.
21. *Serra M., Arenal R., Tenne R.* An overview of the recent advances in inorganic nanotubes // Nanoscale. 2019. V. 11. № 17. P. 8073–8090.
22. *Sheinerman A.G.* Mechanical properties of metal matrix composites with graphene and carbon nanotubes // Phys. Met. Metallogr. 2022. V. 123. № 1. P. 57–84.
23. *Liu D.X.* Microstructures, properties and strengthening mechanisms of titanium matrix composites reinforced by in situ synthesized TiC and unreacted carbon nanotubes // Phys. Met. Metallogr. 2021. V. 122. P. 1551–1560.
24. *Zhou J., Dong J.* Vibrational properties of single-walled gold nanotubes from first principles // Phys. Rev. B. 2007. V. 75. P. 155423.
25. *Cai Y., Zhou M., Zeng M., Zhang C., Feng Y.P.* Adsorbate and defect effects on electronic and transport properties of gold nanotubes // Nanotechnology. 2011. V. 22. P. 215702.
26. *Liu Q., Xu C., Wu X., Cheng L.* Electronic shells of a tubular Au_{26} cluster: A cage-cage superatomic molecule based on spherical aromaticity // Nanoscale. 2019. V. 11. № 28. P. 13227–13232.
27. *Ono S., Yoshioka H.* Breakdown of continuum elasticity due to electronic effects in gold nanotubes // arXiv: 2411.08289. 2024.
28. *Senger R., Dag S., Ciraci S.* Chiral single-wall gold nanotubes // Phys. Rev. Lett. 2004. V. 93. P. 196807.
29. *Goduljan A., Juarez F., Mohammadzadeh L., Quaino P., Santos E., Schmickler W.* Screening of ions in carbon and gold nanotubes – A theoretical study // Electrochem. commun. 2014. V. 45. P. 48–51.
30. *Pathania Y., Kapoor P.* Variation in gold monolayer properties on interaction with DNA/RNA nucleobases useful for DNA sensing // Mater. Sci. Eng. B. 2023. V. 288. P. 116152.
31. *Yang X., Dong J.* Geometrical and electronic structures of the (5, 3) single-walled gold nanotube from first-principles calculations // Phys. Rev. B. 2005. V. 71. P. 233403.
32. *Nhat P.V., Si N.T., Nguyen M.T.* Structural evolution and stability trend of small-sized gold clusters Au_n (n = 20-30) // J. Phys. Chem. A. 2020. V. 124. P. 1289–1299.
33. *Flores M.A., Menéndez-Proupin E.* Spin-orbit coupling effects in gold clusters: The case of Au_{13} // J. Phys. Conf. Ser. 2016. V. 720. P. 012032.

34. *Yakovkin I.N., Petrova N.V.* A DFT study of the proximity effect in the spin-orbit coupling in Au/graphene, Au/silicene, and Bi/silicene bilayers // Phys. Lett. Sect. A Gen. At. Solid State Phys. 2024. V. 506. P. 129475.
35. *Sozykin S.A., Beskachko V.P.* Electronic structure of achiral gold nanotubes // Phys. E Low-Dimensional Syst. Nanostructures. 2020. V. 115. P. 113686.
36. *Sozykina E.R., Sozykin S.A.* Atomic and electronic structures of chiral gold nanotubes // Bulletin of SUSU. Ser. "Mathematics. Mechanics. Physics". 2022. V. 14. № 4. P. 59–64.
37. *Mironov G.I., Sozykina E.R.* Electronic properties of gold nanotubes (5, 3) and (5, 0) in the Hubbard model in the static fluctuation approximation // Low Temp. Phys. 2019. V. 45. № 1. P. 113–117.
38. *Kresse G., Furthmuller J.* Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set // Phys. Rev. B. 1996. V. 54. P. 11169.
39. *Sozykin S.A.* GUI4dft – A SIESTA oriented GUI // Comput. Phys. Commun. 2021. V. 262. P. 107843.
40. *Ganose A.M., Jackson A.J., Scanlon D.O.* sumo: Command-line tools for plotting and analysis of periodic *ab initio* calculations // J. Open Source Softw. 2018. V. 3. P. 717.
41. *D'yachkov P.N., Lomakin N.A.* Simulation of spin selectivity of electrical conductivity of chiral platinum nanotubes // Russ. J. Inorg. Chem. 2023. V. 6. № 4. P. 424–429.