



Density-functional study of the pure and palladium doped small copper and silver clusters



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ABSTRACT

The size-dependent properties of small pure copper and silver clusters and their alloys with one and two palladium atoms are studied by using full-potential density functional computations. The stable isomers of these clusters are identified and their magic numbers are determined via the analysis of the second difference of their minimized energy. We discuss that the doped Pd generally prefers the high coordination sites of the pure cluster. It is argued that Pd doping influences the structural cross over of these clusters. The GW correction is applied for more accurate determination of the electronic structure of the systems.

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1. Introduction

Noble metal nanoclusters are currently attracting a great deal of attention within both experimental and theoretical communities, due to their interesting structural and electronic properties and promising technological applications in nano electronics, nano optics, biological sensing, catalysis, and biomedicine [1–4]. While transition metal ions may induce health and environmental problems [5], noble metal nanoclusters exhibit lower toxicity and hence more biocompatibility. Noble metal nanoclusters are alloyed with palladium atoms to improve their catalytic activity [6,7]. In recent years, extensive computational studies have been devoted to properties of pure noble metal clusters [8–10], although less information is available about structural and electronic properties of the corresponding bimetallics [11,12].

Among noble metal based bimetallic nanoclusters, copper and silver based nano-alloys have been studied considerably less than gold based bimetallic nanoclusters. Wang et al. [13] and Romanowski et al. [14] used density functional (DFT) computations to study AgPd and CuPd dimers and their interaction with H₂. Other calculations have been performed on Cu–Pd trimers and their interaction with molecular and atomic oxygen [15]. The stable geometry of small Ag_nPd_m clusters up to five atoms were found to transform from two-dimensional to three-dimensional as the Pd

content increases [16]. Zhao et al. performed first-principles calculations to study the effects of Pd doping on structural and electronic properties of Ag_nPd ($n \leq 5$) clusters and their mono hydrides [17]. Efremenko et al. [18] have studied the geometric structures and electronic properties of the Pd_nCu_m ($n + m \leq 6$) clusters using DFT. The obtained results show that stability of nanoclusters of the same shape and composition increases linearly with increasing number of PdCu bonds. Up to our knowledge, there is no report on magic number, vibrational spectra, and many body corrected electronic structure of small Pd doped Ag and Cu clusters.

In this paper, quantum mechanical calculations are employed to study pure M_n (M = Ag, Cu) and doped M_{n-m}Pd_m ($n \leq 9$, $m = 1, 2$) clusters and investigate the behaviour of their structural, electronic, and vibrational properties as a function of size. The rest of the paper is organized as follows. In Section 2, we give a brief introduction of the computational method used in this work. Then in Section 3, atomic dimers are investigated with several exchange-correlation functional to select the proper one for our calculations. Next section involves the results of our search for lower energy structures of the selected nano-clusters. In Section 4, the structural, electronic, magnetic and vibrational properties of the most stable clusters are presented. Finally, we will summarize our findings in the last section.

2. Method

All presented calculations are performed in the framework of the spin-polarized Kohn-Sham density functional theory by using the all electron full-potential code FHI-AIMS [19]. This package

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Table 1

Calculated equilibrium bond length r_e (Å), binding energy E_b (eV/atom) and harmonic vibrational frequency ω (cm^{-1}) of the Cu_2 , Ag_2 , Pd_2 , CuPd , and AgPd dimers. The Cu_2 and Ag_2 dimers are calculated in four different exchange-correlation (XC) functionals. The corresponding experimental values (Expt.) are also given for comparison.

	XC	r_e	E_b	ω
Cu_2	PBE	2.21	−1.13	269
	BLYP	2.23	−1.11	261
	revPBE	2.24	−1.02	259
	PW	2.15	−1.39	299
	Expt.	2.21 [28]	−1.04 [29]	265 [29]
Ag_2	PBE	2.57	−0.91	180
	BLYP	2.60	−0.83	172
	revPBE	2.60	−0.79	171
	PW	2.48	−1.45	270
	Expt.	2.53 [30]	−0.83 [31]	192 [30]
CuPd	revPBE	2.32	−0.79	232
AgPd	PBE	2.56	−0.70	179
Pd_2	PBE	2.49	−0.49	195
	Expt.	2.48 [32]	−0.51 [33]	210 [34]

employs basis sets consisting of atom-centered numerical orbitals of the form:

$$R(r) = \frac{u_i(r)}{r} \quad (1)$$

As the name implies, the radial free atom like orbitals $u_i(r)$ are numerically tabulated and therefore exhibit very high flexibility. The strict localized nature of these basis functions lead to much slower scaling of the computational time versus the system size. The calculations reported here are done with the ‘tier2+spd’, ‘tier1+spd’, and ‘tier2’ basis sets which contain 116, 152, and 45 basis functions for Cu, Ag, and Pd atoms, respectively. All the calculations were carried out in the scalar relativistic limit, while the spin-orbit correction was neglected. A recent computational study on the atomic structure of transition metal clusters concluded that this relativistic term has negligible effect on the relative energy differences of the 4d systems [20].

Geometry optimization is performed by the standard Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [21] with a force accuracy of about 10^{-2} eV/Å. Harmonic frequencies are calculated using the finite displacement of all atomic positions by 10^{-3} Å. The lowest energy structures are confirmed to be the true minima by calculating their vibrational frequencies. The FHI-aims package enables us to describe electronic single-quasiparticle excitations in molecules by using many-body correction GW self-energy [22].

3. Dimers

First we focus on the atomic dimers to select a reliable exchange-correlation (XC) functional for our computations and moreover to gain some insights about interatomic interaction in our systems. The equilibrium bond length, binding energy, and vibrational frequency of the Cu_2 and Ag_2 dimers were calculated by using different XC approximations, including PBE [23], revPBE [24] and BLYP [25] generalized gradient (GGA) functionals and PW [26] local density functional. The obtained results are compared with available experimental data in Table 1. It is seen that PBE, revPBE, and BLYP give significantly more accurate binding energy and vibrational frequency while accuracy of equilibrium bond length is qualitatively the same within LDA and GGA based functionals. In the case of Cu_2 , the overall accuracy of revPBE seems to be slightly better than PBE, while the parameters of Ag_2 within PBE is overall closer to experiment. Although, BLYP gives better binding energy for Ag dimer, for larger silver clusters, other theoretical calculations [27] argue that the BLYP functional fails to predict the correct stable structure of

the system. Therefore, we adapt the PBE and revPBE functionals for calculation of Ag and Cu based clusters, respectively.

For better understanding of the interatomic bonds in our target systems, we calculated the Pd_2 , CuPd , and AgPd dimers and presented their results in Table 1. It is observed that the bond length is increasing in the Cu_2 – CuPd – Pd_2 series while the absolute binding energy and vibrational frequency is decreasing. Hence, Cu–Cu bond has a larger strength and stiffness compared with the Cu–Pd and Pd–Pd bonds. Bond length and normal mode frequencies of AgPd and Ag_2 dimers are almost equal while these are larger than those of Pd_2 dimer. The larger bond length of Ag_2 may be due to the large atomic radius of Ag relative to Pd and Cu atoms. Binding energy of Pd_2 is smaller than that of AgPd which in turn is smaller than Ag_2 dimer.

The Mulliken population analysis of valence orbitals shows that Cu and Ag have a similar electronic configuration of $s^{0.94}p^{0.05}d^{10.01}$ in the Cu_2 and Ag_2 dimers. Comparing this configuration with the free Cu and Ag atoms electronic configuration ($s^1p^0d^{10}$) evidences a small *spd* hybridization in these dimers. On the other hand, comparing the electronic configuration of Pd in the Pd_2 dimer ($s^{0.58}p^{0.05}d^{9.37}$) with the free Pd atom ($s^0p^0d^{10}$) indicates a significant *spd* hybridization in the palladium dimer. The reason is that the valence shell of the free Pd atom is composed of fully occupied and fully unoccupied orbitals and hence interatomic bonding between palladium atoms requires significant promotion of electrons from the occupied *d* states to the unoccupied *s* shell. While, the valence shell of the free Cu and Ag atoms has a half filled *s* orbital which is used for interatomic bonding. It is also found that the charge transfer in the Pd–Cu and Pd–Ag bonds happens from Cu and Ag to the more electronegative Pd atom.

4. Stable isomers

In order to investigate properties of atomic clusters, the first essential step is identification of the lowest energy structure of the clusters. Therefore, we performed a careful search for the stable structure of the pure and doped clusters. In the case of the pure clusters, several probable atomic configurations of the clusters taken from various references were included in our manual structure search. After accurate atomic relaxation of the probable configurations and comparing their minimized total energies, the lowest energy isomers of the pure Cu_n and Ag_n clusters ($n \leq 9$) were identified and sketched in Figure 1. These findings are in agreement with a recent study on silver clusters [35]. Because of the presence of two different atoms, the process of finding the lower energy structures of the doped clusters is more complicated than the pure clusters. Therefore, for finding the most stable structures of the palladium doped clusters, we tried to limit our search to the more stable configurations proposed by previous studies on the Cu_nPd_m ($n + m \leq 6$) [18] and Ag_nPd_m ($n + m \leq 5$) [36,16] clusters. The resulting most stable isomer of the doped clusters are presented in Figure 1. It is seen that the most stable $\text{M}_{n-2}\text{Pd}_2$ clusters are made of the maximum number of pyramids and moreover the two Pd atoms in these systems tend to bond together. These observations were used for obtaining the most stable structure of the M_6Pd_2 and M_7Pd_2 clusters.

The results show that up to the size of 6 (heptamer), pure clusters prefer 2 dimensional (2D) planar structures while larger clusters stabilize in 3D geometries. In order to understand the origin of this 2D–3D cross over, we analyzed the average bond length (d) and the average coordination number of atoms (n_c) in the most stable 2D and 3D isomers of the Cu_n and Ag_n clusters (Figure 2). It is seen that the 2D isomers have lower average coordination and shorter average bond length, because the valence charge density of these systems is distributed among lower number of bonds,

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