



Aspects of bonding in small gold clusters



Xiao-Gen Xiong^{a,b,1}, Wen-Hua Xu^{a,2}, Jun Li^{a,*}, Pekka Pyykkö^{b,**}

^a Department of Chemistry, Tsinghua University, 100 084 Beijing, China

^b Department of Chemistry, University of Helsinki, P.O.B. 55, 00014 Helsinki, Finland

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ABSTRACT

A DFT-level study on neutral or charged Au_n clusters at relativistic and non-relativistic (R/NR) levels confirms the previously suggested relativistic origin of the planar structures. In addition, a number of potentially new aspects are observed: (1) The symmetries with a large relativistic contribution to the orbital interaction term, ΔE_R^{orb} , are those, already spanned by the NR 6s orbitals, but now with strong 6s–5d hybridization. (2) All planar structures have an ‘off-plane σ ’ (aka δ) bonding orbital. (3) Many molecular orbitals can be seen as linear combinations of the a_1 orbitals of the smallest triangular units.

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1. Introduction

A substantial literature exists on small gold clusters, with or without ligands. For some reviews, see Häkkinen [1] or Pyykkö [2,3]. The main valence orbital of Au_n^q ($q = -1, 0, +1$) compounds is thought to be the 6s, with the 5d being a core orbital. Actually, substantial 6s–5d hybridization occurs in the relativistic case, because of the stabilization the Au 6s and destabilization of the 5d by relativistic effects.

The Au_n^q clusters prefer a planar structure up to an n of 11, 10 and 7 for q of $-1, 0$ and $+1$, respectively (see Ref. [3]). Many of the planar structures have been confirmed to be the most stable isomers through both experimental and computational studies [4–8]. For even larger clusters, combined experimental and computational results show the 3D structures are more favorable [9–12]. A famous example is the tetrahedral Au_{20} cluster, whose structure is a fragment of fcc bulk gold [9]. A comparison of relativistic (R) and non-relativistic (NR) methods showed that relativistic effects favour planarity [13], or ‘small coordination numbers’, in general [14]. A special case of $[Au_7]^-$ was reported by Häkkinen and the planarity was attributed to strong sd hybridization and d – d interaction.

[13] The sd hybridization is also mentioned by Furche et al. [15]. Fernández et al. [16] in particular evoke the role of the doughnut-like $5d_{zz}$ –6s orbital. The bonding in Au_6 is analyzed in detail in terms of Au_3 triangles by Zhai et al. [17] (see Fig. 7), and the bonding in Au_n^+ by Yang et al. [18]. Note that a bulk compound based on Au_3^+ was just reported by Robilotto et al. [19].

For the structural differences given by different functionals, see Ferrighi et al. [20] or Mantina et al. [21]. The qualitative understanding is that the sd hybridization will favour directional bonding and hence lower symmetry [21]. Grönbeck and Broqvist [22] evoke d – d overlap, d -electron delocalization and also polarization effects of the 5s5p semicore states. For the d – d interaction, see also Fa et al. [23]. Concerning spin-orbit (SO) effects, Johansson et al. [6] find they favour 3D over 2D for anions around Au_{12}^- .

2. Results

The structures of the species considered are shown in Fig. 1. Closed-shell states were chosen for all these clusters. Planarity is more favorable for all cases and the results agree with previous reports [7,24–27]. The planar Au_8 with D_{4h} symmetry is 0.41 eV lower than the non-planar structure with T_d symmetry, which is consistent with benchmark CCSD(T) calculations with large basis sets and core-valence correlation whose energy difference between these two isomers is 0.65 eV [27].

2.1. The bonding energies

The bonding energies of the present closed-shell clusters with respect to separated atoms are given in Table 1. As ADF uses spin-restricted energies of average-of-configuration (AOC) atoms

* Corresponding author. Tel.: +86 10 62795381; fax: +86 10 62777472.

** Corresponding author. Tel.: +358 9 19150171.

E-mail addresses: junli@tsinghua.edu.cn (J. Li), Pekka.Pyykko@helsinki.fi (P. Pyykkö).

¹ Present address: Division of Nuclear Materials Science and Engineering, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China.

² Present address: Department of Chemistry and Materials Science, Northwest University, Xi'an 710069, China.

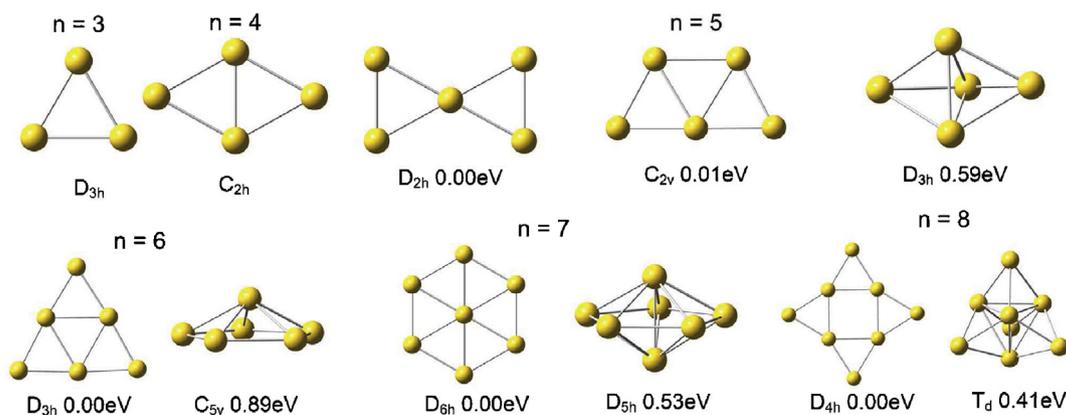


Fig. 1. The structures of the closed-shell gold clusters. For Au_5^+ , Au_6 , Au_7^+ and Au_8 both the 2D and 3D alternatives are shown.

Table 1

Bonding energy analysis of gold clusters (eV). The SR-ZORA optimized geometries were used in the SO-ZORA single-point calculations. The last column includes spin-orbit effects.

System		ΔE_{SR}			ΔE_{SO}^a
		Steric ^b	Orbital ^b	Total ^a	
Au_2	1D($D_{\infty h}$)	1.84	-4.48	-2.30 ^c	-2.36 ^c
Au_3^+	2D(D_{3h})	3.92	-0.93	-5.89	-6.15
Au_4	2D(D_{2h})	5.96	-12.77	-6.11	-6.70
Au_5^+	2D(D_{2h})	7.76	-9.70	-10.57	-10.87
	3D(D_{3h})	8.58	-9.94	-9.99	-10.48
	2D-3D	-0.82	0.24	-0.58	-0.39
Au_6	2D(D_{3h})	10.77	-23.25	-11.42	-11.83
	3D(C_{5v})	10.33	-21.91	-10.53	-10.99
	2D-3D	0.44	-1.34	-0.89	-0.84
Au_7^+	2D(D_{6h})	13.42	-20.88	-15.73	-16.26
	3D(D_{5h})	13.90	-20.83	-15.20	-15.92
	2D-3D	-0.48	-0.05	-0.53	-0.34
Au_8	2D(D_{4h})	14.95	-32.19	-15.83	-16.39
	3D(T_d)	16.26	-33.09	-15.42	-16.17
	2D-3D	-1.31	0.90	-0.41	-0.22

^a Atomic correction terms are included to obtain the 'real' bonding energy. For cations, the first IE (ionization energy) of Au is also considered.

^b A spherically symmetric and spin-restricted Au atom is used as the reference.

^c The experimental D_e is 2.302 eV.

as fragments, in order to obtain the 'real' bonding energy, atomic correction terms has been applied for the true Au atom ground state [28]. For cations, the bonding energy has also been corrected with calculated Au first ionization energy. The total bonding energy can be separated to Pauli repulsion, electrostatic interaction and orbital interaction terms [29].

$$\Delta E_{Bonding} = \Delta E_{Steric} + \Delta E_{OrbInt} = \Delta E_{Elstat} + \Delta E_{Pauli} + \Delta E_{OrbInt} \quad (1)$$

The relativistic changes of these bonding energies are given in Table 2. For the clusters we studied here, the planar structures have large steric repulsions compared to the three-dimensional structures, but they also have large orbital interaction energies. Note that the relativistic contributions to the 2D-3D energy difference in Table 2 are more negative, than the total values in Table 1. At the scalar-relativistic level, the clusters we studied here prefer the planar structures. But at the non-relativistic level, taken the Au_8 as example, the three dimensional structure with T_d symmetry is more stable than the planar structure with 0.94 eV. The planar (2D) structures are driven by relativistic effects; the NR case prefers 3D. We next study the orbital interactions of various symmetries. Through the group-theory method, those spanned by the Au 6s orbitals for each planar gold cluster can be deduced as shown in

Table 2

The scalar relativistic changes of bonding energy (eV).

System		ΔE_R		
		Steric	Orbital	Total
Au_2	1D($D_{\infty h}$)	0.40	-0.86	-0.46
Au_3^+	2D(D_{3h})	0.85	-0.13	0.72
Au_4	2D(D_{2h})	1.01	-2.02	-1.01
Au_5^+	2D(D_{2h})	1.51	-1.53	-0.02
	3D(D_{3h})	0.96	-0.48	0.48
	2D-3D	0.55	-1.05	-0.50
Au_6	2D(D_{3h})	1.50	-3.27	-1.77
	3D(C_{5v})	1.25	-2.43	-1.18
	2D-3D	0.25	-0.84	-0.59
Au_7^+	2D(D_{6h})	1.80	-2.20	-0.41
	3D(D_{5h})	0.64	-0.01	0.63
	2D-3D	1.16	-2.19	-1.04
Au_8	2D(D_{4h})	1.98	-4.54	-2.56
	3D(T_d)	0.59	-1.42	-0.82
	2D-3D	1.39	-3.12	-1.74

Table 3

6s-Based molecular orbitals in planar gold clusters.

System	Symmetry	All 6s orbitals	Occupied 6s orbitals
Au_2	$D_{\infty h}$	$\sigma_g + \sigma_u$	$(4\sigma_g)^2$
Au_3^+	D_{3h}	$a_1' + e_1'$	$(5a_1')^2$
Au_4	D_{2h}	$2a_g + b_{2u} + b_{3u}$	$(5a_g)^2(7b_{3u})^2$
Au_5^+	C_{2v}	$3a_1 + 2b_2$	$(9a_1)^2(15b_2)^2$
	D_{2h}	$2a_g + b_{1g} + b_{2u} + b_{3u}$	$(5a_g)^2(8b_{2u})^2$
Au_6	D_{3h}	$2a_1' + 2e'$	$(5a_1')^2(12e')^4$
Au_7^+	D_{6h}	$2a_{1g} + e_{2g} + b_{1u} + e_{1u}$	$(4a_{1g})^2(5e_{1u})^4$
Au_8	D_{4h}	$2a_{1g} + b_{1g} + b_{2g} + 2e_u$	$(5a_{1g})^2(11e_{1u})^4(7b_{2g})^2$

Table 3. An analysis of the relativistic contributions in Table 4 shows that these 6s-containing molecular orbitals predominate. Even at the non-relativistic level, most of the bonding energies also come from 6s-based orbitals.

Table 4

Orbital interaction energy and the contribution of s-based orbitals for planar gold clusters (eV).

	Au_2	Au_3^+	Au_4	Au_5^+	Au_6	Au_7^+	Au_8
$\Delta E_{bonding,6s}^{SR}$	-4.33	-0.70	-12.21	-9.34	-22.38	-23.10	-31.09
$\Delta E_{bonding,6s}^{NR}$	-3.53	-0.59	-10.32	-7.90	-19.27	-19.88	-26.74
$\Delta E_{bonding}^{SR}$	-4.48	-0.93	-12.77	-9.70	-23.25	-20.88	-32.19
$\Delta E_{bonding}^{NR}$	-3.63	-0.81	-10.75	-8.17	-19.98	-18.68	-27.65

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