# Aurophilic attractions between a closed-shell molecule and a gold cluster<sup> $\dagger$ </sup>

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The attractions between a closed-shell gold cluster and a closed-shell Au(I) molecule are theoretically studied, and related to monomer properties. The results suggest that the Au(I) mainly interacts with the nearest gold atoms and that the interaction is roughly proportional to the number of nearest neighbours. Different functionals are compared. The SCS-MP2 results are close to the CCSD(T) ones for the systems studied. The question of ionic contributions to the stability of 'staple' structures is raised.

# 1 Introduction

The 'aurophilic' <sup>1</sup> or 'metallophilic' <sup>2</sup> attraction is a relatively recently identified cohesive contribution that appears to occur between two closed-shell metal atoms inside a molecule, or between such atoms in different molecules. The system can contain dimers, oligomers, infinite chains, or infinite, two-dimensional sheets, such as the Au(I) planes in solid AuCN. The gold compounds usually have Au(I) although Au(III) may occur as well.

The earlier literature in this area was summarised in our reviews<sup>3–6</sup>, and in the introduction of our recent paper on the dependence of aurophilicity in [ClAu*L*]<sub>2</sub> systems on the neutral ligand, *L*.<sup>7</sup>. Some key steps were the identification of the attraction as an electron correlation effect<sup>8,9</sup>, the London-like  $R^{-6}$  behaviour at large distances<sup>10,11</sup> and the detailed analysis of the dispersion-type plus other bonding contributions using localised orbitals<sup>12,13</sup>. In the virtual one-electron excitations, the initially occupied orbital *i* is typically an Au 5d, but the final orbital *f* may have considerable ligand character<sup>8,12</sup>. In that sense the idea of a monoatomic 'metallophilicity' at each monomer is not accurate.

The metallophilic interaction strength oscillates along the series MP2, MP3, MP4, CCSD,  $CCSD(T)^{13-15}$ . This had an unexpected consequence: While the relativistic effects strengthened the interaction at MP2 level<sup>14</sup>, as verified by O'Grady and Kaltsoyannis<sup>16</sup>, they found that at the higher correlated levels QCISD, CCSD and CCSD(T) the interaction weakened, when passing from Ag to Au,

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which is almost tantamount to adding relativistic effects to non-relativistic gold, silver being approximately 'non-relativistic gold' <sup>17</sup>. The trends in perpendicular  $[XAuL]_2$  model systems<sup>2,7</sup> suggest that softer 'halogens' X will have stronger aurophilic interactions. As a final link to metallophilicity, we quote the so-called 'no-pair' bonding in systems like a predicted, tetrahedral S = 2 high-spin energy minimum of Cu<sub>4</sub>. In that case there is no electron-pair bonding, all valence electrons having the same spin, but electron correlation from the 3d<sup>10</sup> shell explains most of the bonding which is calculated to be 19 kJ/mol per Cu-Cu pair<sup>18</sup>.

What seems to be missing, are theoretical studies on metallophilic attractions for systems that contain, on one hand, a basically closed-shell gold cluster, in an average Au oxidation state far below +I and, on the other hand, a closed-shell molecular group, containing Au(I), such as the bridging surface groups (called *staples*, for a sketch, see Figure 8 below), of the type [-SR-Au-SR-]<sup>-</sup> in recent cluster work. The need for such studies appeared, when it was found that many thiolate-protected gold clusters consisted of a compact inner Au<sub>n</sub> cluster and outer groups of that type, or of the longer [-SR-Au-SR-Au-SR-]<sup>n-</sup> type. The first example was the [Au<sub>102</sub>(SR)<sub>44</sub>], experimentally studied by Jadzinsky et al.<sup>19</sup>. Theoretical modelling of that experimental structure was undertaken by Walter et al.<sup>20</sup> using density functional theory (DFT), and gave a closely similar result. Another example is [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>-</sup>, where both experiments<sup>21</sup> and DFT<sup>22</sup> suggest a formal inner Au<sup>5+</sup><sub>13</sub> inner icosahedron and an outer layer containing [(SR-Au-SR-Au-SR)]<sup>6-</sup> units.

While DFT describes well the covalent Au-S bonds of the system and also the Coulomb attractions between the cationic core and the anions on the surface – an aspect not explicitly discussed yet – regular exchange-correlation (XC) functionals, commonly used today, are not able to reliably describe the predominantly dispersion-type interactions. Therefore even the simplest model studies on the aurophilic interactions between a formal Au(I) and a gold cluster are of interest. A typical question to ask is, will the molecular Au(I) center interact with only the nearest gold atoms of the cluster, or with the entire cluster, and what is the order of magnitude of the total interaction. A further possible bonding contribution are the different induction terms.

We address here the simplest possible model cases, modelling the inner part by Au<sub>2</sub>, Au<sub>6</sub> or Au<sub>8</sub> and the outer part with AuH or AuCl<sub>2</sub><sup>-</sup>. The wave-function theoretical (WFT) methods applied range from MP2 to CCSD(T). A number of density functional theories are tested, as well. The calculations were performed using the codes Molpro2010<sup>23</sup> and NWChem6.0.<sup>24</sup>. The latest Au pseudopotential of Figgen et al.<sup>25</sup> and the related, correlation-consistent basis sets of Peterson and Puzzarini<sup>26</sup> were used. For comparison, an MP2-level study of the basis-set limits for two other aurophilic models exists<sup>27</sup>, including an extrapolation to the infinite-basis limit.

# 2 Results

#### 2.1 The gold hydride models

One of the simplest models for intermolecular aurophilicity is the end-on Au-Au ... Au-H. An even simpler system is the monomolecular  $C_{2\nu}$  HAu<sub>2</sub><sup>+</sup> of Berger<sup>28</sup>.

Recall also the mass-spectroscopic observation of linear AuAuH<sup>-</sup> and AuHAu<sup>-</sup> by the group of L. S. Wang<sup>29</sup>, the matrix-spectroscopic observations of further, neutral gold hydride species, such as (H<sub>2</sub>)AuH and (H<sub>2</sub>)AuH<sub>3</sub> by the group of Andrews<sup>30–33</sup> and the theoretical study on AuH<sub>3</sub><sup>34</sup>.

**2.1.1 Calibration results on monomers.** Some calibration results for the monomers are given in Table 1.

**Table 1** Calculated bond lengths,  $R_e$ , (in picometers, pm) for the monomers at triple-zeta level.

Case	Method	R <sub>e</sub>
AuH	MP2	149.1
	SCS-MP2	149.1
	CCSD	152.5
	CCSD(T)	152.3
	Exp	152.4
$Au_2$	MP2	242.9
	SCS-MP2	242.9
	CCSD	249.1
	CCSD(T)	248.4
	Exp	247.2



**Fig. 1** The various wave-function-theory (WFT) curves for Au-Au...Au-H, **1**. The distance R is the intermolecular, Au<sub>2</sub>...Au<sub>3</sub> one.

**2.1.2** Linear  $Au_2$  ... AuH, 1. The structures for the dimer models studied are shown in Figure 2

The end-on Au<sub>2</sub> results are shown in Table 2.

We note that CCSD gives for 1 the weakest interaction, while CCSD(T) and  $SCS-MP2^{35}$  are comparable, thus justifying SCS-MP2 as a 'poor man's



Fig. 2 The structures for the dimer models 1 (a), 2 (b), 3a (c), 3b (d), 3c (e), 4 (f), 5 (g) and 6 (f).

Case	Method	$R_e$	$D(R_e)$
1	MP2	265.7	34.8
	SCS-MP2	278.7	20.6
	CCSD	280.8	10.7
	CCSD(T)	276.7	20.5
	B3LYP	284.3	14.3
	revPBE	277.2	15.7
	BLYP	280.0	20.4
	TPSSh	268.5	25.9
	SV-BP	270.5	29.5
	PBE	269.2	31.4
	TPSS	267.3	32.2
	PW91	268.5	33.7
	M06	274.9	34.3
	Χα	264.5	57.7
	SVWN	259.1	68.1

**Table 2** Aurophilic interaction distances,  $R_e$ , (in pm) and energies,  $D(R_e)$ , (in kJ/mol) for end-on Au<sub>2</sub> ...AuH **1**.

CCSD(T)'. MP2 gives the strongest interaction. We choose SCS-MP2 as a tool for studying larger systems.

The side-on planar  $(Au_2)$ ...AuH collapses to the single molecule 2, consisting of an Au<sub>3</sub> triangle, with an H bound to a corner, and was omitted.

#### 2.2 Comparison with DFT

The interaction energies for **1** with various functionals are given in Table 2 and Figure 3, in order of strength. We conclude that, for the particular model system **1**, B3LYP and revPBE underbind, while the last five functionals, notably PBE mostly used by Häkkinen's group (see e.g. refs.<sup>20,22,36</sup>) overbind, in this case by about 10 kJ/mol or 50%. Wang and Schwarz<sup>37</sup> find for a number of aurophilic systems that B3LYP underbinds while the S and SV LDF overbind, in line with the present results.

#### 2.3 The electron-localization functions

The 'electron-localization functions' (ELF) for species 1 and 2 are shown in Fig. 4. They also correspond to closed-shell and partially covalent interactions between the Au<sub>2</sub> and AuH moieties, respectively.

## 2.4 The large-*R* limit

It is often instructive to relate the potential-energy curve V(R) to the various terms  $V = C_n/R^n$  at the large-*R* limit <sup>7,10,11</sup>. We do it here for the collinear Au-Au...Au-H (= A...B) case. Denoting the dipole and quadrupole moments by  $\mu$  and  $\Theta$ , respectively, the formulae of Stone <sup>38</sup> and Muñiz et al.<sup>7</sup> yield (here in a.u.)

$$C_4 = 3\Theta^A \mu^B, \tag{1}$$

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Fig. 3 The various DFT curves versus the CCSD(T) one for Au-Au...Au-H, 1

**Fig. 4** The ELF:s for species **1** (a) and **2** (b).



$$C_5 = 6\Theta^A \Theta^B, \tag{2}$$

$$C_6 = -\frac{1}{2} \frac{I_A I_B}{I_A + I_B} [\alpha_{\perp}^A \alpha_{\perp}^B + 2\alpha_{\parallel}^A \alpha_{\parallel}^B].$$
(3)

Denoting the distance between the  $Au_2$  midpoint and the  $Au_3$  atom as R, we can write the dominant, repulsive, long-distance interaction as

$$V_4(R) + V_5(R) = C_4/(R + x_B)^4 + C_5/R^5$$
(4)

while for the short-distance attraction we can experiment with a single Au<sub>2</sub> polarisability,  $\alpha$ , at the molecular midpoint, or half of it on each Au atom:

$$V_6^{\text{Single}}(R) = -C_6/R^6, \tag{5}$$

$$V_6^{\text{Split}}(R) = -\frac{1}{2}C_6/(R - x_A)^6 - \frac{1}{2}C_6/(R + x_A)^6.$$
 (6)

$$V(R) = V_4(R) + V_5(R) + V_6(R)$$
(7)

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The required monomer properties are given in Table 3. The tacit assumptions are that the AuH dipole moment and the Au<sub>2</sub> quadrupole moment reside at the molecular midpoints, while the AuH quadrupole moment and polarisability reside at gold atom 'Au<sub>3</sub>'. The obtained, total interactions are compared in Figures 5 and 6. The conclusion becomes that the 'split' polarisabilities perform quite well for 1, at the MP2 level used. Moreover, note that this 'local London' estimate is not far from the MP2  $V(R_e)$ , the work done against the intermolecular Pauli repulsion being small. One can almost continue the large-*R* extrapolation to  $R_e$ . To the contrary, if one tries to do the same with the single polarisability of the entire Au<sub>2</sub> molecule, the interaction remains much too weak, as seen from Figures 5 and 6.

It would be premature to characterise this success of the 'split model' as an example on local, virtual surface plasmons, the atom  $Au_1$  of the gold cluster representing the bulk atoms and  $Au_2$  representing the surface atoms of the gold cluster, nearest to the approaching Au(I) atom.

**Table 3** MP2-level monomer properties, used for fitting the aurophilic attraction potential, V(R) in Figures 5, 6. 'PW' = present work. If not otherwise said, atomic units are used.

Molecule	<i>R<sub>e</sub></i> /pm	μ	Θ	$lpha_\parallel$	$lpha_{\perp}$	$\alpha_{av}$	Source
Au <sub>2</sub>	242.6	-	6.272	49.38	112.28	70.35	PW
				65.7	114.2	81.9	а
AuH	151.	0.405	2.809	36.06	41.65	37.92	PW
<sup><i>a</i></sup> Ref. <sup>39</sup> , Dirac-Fock level.							



**Fig. 5** The long-distance repulsive interaction for Au-Au...Au-H, **1**. The points come from SCS-MP2 calculations. The curves correspond to Eqs. (5,6).

10

R /Å

0.01

5

20



**Fig. 6** The short-distance interaction for Au-Au...Au-H, **1**. The points come from SCS-MP2 calculations. The curves correspond to Eqs. (5,6).

### 2.5 Larger models

We also considered the case  $Au_2 \dots AuCl_2^-$  in three geometries, all  $C_{2\nu}$ , see Figure 2. The results are given in Table 4. The T-shaped planar structure **3a** has an SCS-MP2 interaction energy of -122 kJ/mol. The planar **3b** and the perpendicular **3c** have energies in the aurophilic range. Moreover, these energies between one Au(I) and two Au(0) of **3** are larger than those between one Au(I) and one nearest-neighbour Au(0) of the previous example **1**.

**Table 4** Aurophilic interaction distances,  $R_e$ , (in pm) and energies,  $D(R_e)$ , (in kJ/mol) for larger models at SCS-MP2 level. Here *n* is the number of nearest-neighbour Au atoms to the approaching Au atom and  $R_e$  is taken as the distance between them.

Case	п	R <sub>e</sub>	$D(R_e)$
3a	1	259.7	122
3b	2	299.8	54
3c	2	297.1	30
4	3	281.6	122
5	4	280.9	132
6	4	350.3	76

The Au(I) of the approaching AuH unit has three nearest Au neighbours in Au<sub>6</sub> in system **4** and four ones in Au<sub>8</sub> in system **5**. The increase of the interaction energy with the number of nearest neighbours is shown in Figure 7.

A further aurophilic model where one Au(I) interacts with an Au<sub>n</sub> unit (n > 2), we let the AuCl<sub>2</sub><sup>-</sup> interact with a quasiplanar  $D_{4h}$  Au<sub>8</sub> in **6**. The structure is given in Figure 2 and the interaction described in Table 4.



Fig. 7 The increase of the  $[H-Au]...[Au_{2n}]$  interaction energy with the number of nearest neighbours, *n* for species 1, 4 and 5. The points come from SCS-MP2 calculations.

# 3 A bond-energy-plus-Coulomb model for the staple-covered clusters

It is interesting to ask whether differential Coulomb effects could contribute to the transition from a homogeneous gold cluster, covered by simple thiolates,  $[Au_N (SR)_{2M}]$  to an  $[Au_{N-M}]@[SRAuSR]_M$  'core+shell' structure. Note that the former S atoms are two-coordinated and the latter three-coordinated. This argument for the L = S-Au-S 'staples' can be generalized for the L = S-Au-S staples.

To demonstrate the principle, let M = 1 and consider the bond energies (all taken as positive) in Figure 8. They yield the thermochemical diagram in Figure 9, from which we can read out the energy change

$$\Delta E = 2E_1 - 2E_2 + E_{Au} + IP - EA - E_C - 2E_3 - E_4.$$
(8)

Here  $E_1$ ,  $E_2$ ,  $E_3$  are the energies of the Au-S bonds, explained in Figure 8, *IP* is the ionisation potential of the Au<sub>N-1</sub> cluster and *EA* the electron affinity of Au(RS)<sub>2</sub>.  $E_4$  is the aurophilic attraction energy between the ligand Au atom and the remaining cluster and  $E_C$  the Coulomb attraction between the staple ligand and the Au<sub>N-1</sub> cluster.

Some 'educated guesses' for these bond energies can be obtained from the compilation of Luo<sup>40</sup>. A typical Au-S bonding energy is quoted as 253 kJ/mol but we can let the terms  $2E_1$  and  $2E_2$  cancel out. For the third, Au-S, bond to two-coordinated sulphur, Luo quotes values of the order of 50 kJ/mol, taken as estimate for  $E_3$ . Our own current estimate for  $E_4$  in system '4' is 76 kJ/mol. A typical Au-Au bond energy  $E_{Au}$  is 225 kJ/mol. The adiabatic *IA* and *EA* for Au<sub>9</sub> are reported as 602 and 368 kJ/mol, respectively<sup>41</sup>. Then Eq. (8) estimates that  $\Delta E$  turns negative for an additional Coulomb attraction,  $E_C$ , of only 225 +602 -368 -100 -76 = 283 kJ/mol. This would correspond to two opposite unit charges



**Fig. 8** A schematic structure for the simplest 'staple' structure on a gold cluster. We denote the bond energies by  $E_2$  for the S-Au(staple),  $E_3$  for S-Au(cluster) and  $E_4$  for the aurophilic interaction Au(staple) ...Au(cluster).  $E_C$  is the Coulomb attraction between the staple and the cluster. The Au-S bond energy of the original [(Au<sub>N</sub>)(SR)<sub>2</sub>] cluster is denoted by  $E_1$ .



Fig. 9 A thermochemical diagram for the system in Figure 8.

at a distance of 491 pm. This very rough order-of-magnitude estimate would permit a role for Coulomb interactions between the staples and the core, as one of the driving forces.

P. Pvykkö, University of Helsinki, 2011

# 4 Conclusions

This paper presents more questions than definitive answers. We are not aware of earlier studies on the aurophilic attraction between a closed-shell Au(I) molecular moiety and an Au<sub>N</sub> cluster at WFT level. Even the simplest models considered here may provide valuable calibration points for existing DFT studies. The idea of local virtual excitations in the cluster may be useful. Moreover, the possible role of Coulomb attractions between the staples and the remaining cluster may be worth of future consideration.

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