



A comparative study between post-Hartree–Fock methods and density functional theory in closed-shell aurophilic attraction



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ABSTRACT

The inter- and intramolecular aurophilic $[\text{ClAuPH}_3]_2$, $[\text{S}(\text{AuPH}_3)_2]$ and $[\text{AuPH}_3]_4^{2+}$ interactions were studied using ab initio post-Hartree–Fock and DFT methodologies. The post-Hartree–Fock methods provide results closer to the experimental data than DFT-based methods. It is possible to highlight the results obtained by the SCS-MP2 and CCSD(T) methods. In the classic $[\text{ClAuPH}_3]_2$ dimer, the aurophilic interaction is driven by the induction and dispersion terms. When DFT is used, the best results of geometry and interaction energy are obtained with the PW91 level. We find -D3 Grimme correction, M06HF, M06L, M06 M062X, M052X, CAM-B3LYP and LC- ω PBE provided results of similar accuracy as MP2.

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1. Introduction

It is well established that the attractive interactions between cations with d^8 , d^{10} and s^2 configurations at both the intra- and intermolecular levels lead to the formation of dimers, oligomers, chains, sheets, clusters and nanoparticles [1–8]. This phenomenon is known as metallophilic attraction, and in the particular case of gold, as ‘aurophilic attraction’ [9–15]. These closed-shell interactions are estimated to be energetically similar to hydrogen bonds (20–50 kJ mol⁻¹) in the case of gold(I) and to be weaker for other metals, such as silver(I), copper(I), thallium(I), mercury(II) and platinum(II) [16–19]. In the case of gold, the aurophilic Au–Au interaction has been determined experimentally via solid state X-ray diffraction [1–8] and NMR measurements [20,21]. From a theoretical point of view, the aurophilic attraction has been understood as the contribution of two terms to the equilibrium distance: dispersion and ionic [13]. The relativistic effects contribute 27% to the intermolecular interaction energy [12]. It should be noted that ÓGrady and Kaltsoyannis reproduced the results at the MP2 level but noticed that the higher levels such as CCSD(T) and CCSD, when going from silver to gold, the metallophilic attraction energy suffered a decrease [13]. Moreover, they showed that argentophilic is stronger the aurophilic.

Other reasons for interest in these interactions are due to different characteristics of gold such as the electronic structure of gold

nanoparticles, gold nanoparticle–ligand interactions, the coordination chemistry of gold, gold clusters, and gold-catalyzed organic transformations [22–30]. Moreover, a significant number of studies have discussed the aurophilic interactions coexisting with H-bonding, M– π or π – π attractions, all of which can participate in generating extended, supramolecular structures and nanochemistry [31–35]. The experimental results in many works are explained with theoretical models described at the density functional theory (DFT) level due to the size of the system.

At the theoretical level, the mechanism behind the aurophilic interaction (in general metallophilic) is the dispersion-type (van der Waals) contribution, with additional allowance for virtual charge-transfer terms [13,36–38]. The dispersion interaction is recovered in the electronic correlation. However, it has been stated that all dispersion is correlation but all correlation is not dispersion [15]. Furthermore, not all the localized orbitals involved are purely metal orbitals. A rough first idea of the nature of these interactions can be obtained by comparing calculations carried out at the Hartree–Fock (HF) and post-Hartree–Fock levels of theory, such as second-order Moller–Plesset (MP2) for simplified model systems [39,40]. Although it is known that the MP2 approximation exaggerates such attractive interactions, it gives a good indication of their existence. A more precise post-Hartree–Fock level is CCSD(T), although recently calculations with the spin-component-scaled (SCS) MP2 method have produced results comparable to CCSD(T) at a lower computational cost [41–43]. Thus, SCS-MP2 is considered as an accurate and efficient tool for incorporating electronic correlation to the study of large systems.

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On the other hand, until recently calculations based on DFT for the description of metallophilic attractions were not adequate because the interaction energy near the van der Waals minimum was unreliable. The main reason for that was related to the fact that the specific form of the correlation energy (virtual double-dipole excitations, leading to an R^{-6} power law) was not properly described [11,44–46]. This misbehavior of DFT-based methods, which are not able to reliably describe the predominantly dispersion-type interaction, can be found from the traditional hybrids such as B3LYP and most complete as TPSS or PBE [11]. It is also possible to find methods with similar behavior such as M05-2X and M06-2X of the Truhlar group [47,48]. This situation has been changing in recent years due to several attempts to incorporate a dispersion term by different means. Grimme's group has been one of the first to succeed, including a correction of the DFT total energy with C_6R^{-6} and higher-order atom-atom type corrections [49,50]. Andrejic and Mata have studied the $[\text{ClAuPH}_3]_2$ dimer using PBE with dispersion at the D3 level [51]. They have obtained results similar to the MP2 level. Other theoretical results at the DFT level were obtained using the SAPT (symmetry-adapted perturbation theory) method on the Au_2 , $(\text{AuH})_2$ and $(\text{HAuPH}_3)_2$ systems [37]. Finally, the LC- ω PBE-XDM method has been implemented to study interactions in simple aurophilic dimers $[\text{XAuPH}_3]_2$ ($X = \text{H}, \text{Cl}, \text{Br}, \text{I}$) with the purpose of including dispersion interactions [52].

There is a significant amount of experimental and theoretical studies containing interactions with centres of gold complexes and clusters reported in the literature [53]. Of these, there are two systems that represent intramolecular gold-gold interactions and the covalent bond with aurophilic attraction: A-frame $[\text{S}(\text{AuPH}_3)_2]$ and $[\text{AuPH}_3]_4^{2+}$, respectively. The first complex has been studied with different post-Hartree–Fock methods (MP2, MP3, MP4, CCSD, and CCSD(T)) and DFT geometry of the system [54–56]. The importance of electronic correlation of the Au–Au distance on level dispersion and ionic terms has been shown. The second system, $[\text{AuPH}_3]_4^{2+}$, is the smallest possible polyhedral gold cluster [57–59]. This cluster adopts full tetrahedral symmetry. This cluster is the precursor of nanometer-size larger systems. It has been demonstrated that the covalent Au–Au bond in the $[\text{AuPH}_3]_4^{2+}$ cluster is accentuated by aurophilic interaction [57–59].

The purpose of this study is to quantify the effect of dispersion at the DFT level and compare it with post-Hartree–Fock methods (MP2, SCS-MP2 and CCSD(T)). To demonstrate such an objective we used the classic three simplest models to study the effect of the inter- and intramolecular aurophilic attraction: $[\text{ClAuPH}_3]_2$, $[\text{S}(\text{AuPH}_3)_2]$ and $[\text{AuPH}_3]_4^{2+}$. This will clarify which of the DFT methods are best suited to study gold nanoparticles and clusters.

2. Computational details

First we fully optimized the geometry of the $[\text{ClAuPH}_3]$ monomer at the different theory levels (see Table 1). Then, we used this geometry to study the Au–Au intermolecular interactions in the $[\text{ClAuPH}_3]_2$ dimer (see Fig. 1) with C_2 symmetry (with a 90° dihedral angle) [12]. The $[\text{S}(\text{AuPH}_3)_2]$ (C_{2v}) and $[\text{AuPH}_3]_4^{2+}$ (C_{3v}) models describe the intramolecular Au–Au interaction and the gold bonds in a small cluster, respectively.

The calculations were done using Turbomole version 6.5 [60] and Gaussian 09 [61]. For Au atoms we used the scalar relativistic Stuttgart pseudopotentials (PP): 19 valence-electron (VE) for Au [62]. The calculations have been performed using two different basis sets. For the smaller set (VDZP), two f -type ($2f$) polarization functions were added to Au ($\alpha_f = 0.20, 1.19$) [12], while the second basis set for Au, used as a model for a larger basis sets (AVTZ), was augmented with ($3f2g$) functions ($\alpha_f = 1.41, 0.40, 0.15$; $\alpha_g = 1.20,$

Table 1

Main geometric parameters of the $[\text{AuCl}(\text{PH}_3)]$ monomer model studied. Distances in pm and angles in degrees.

Method	Basis on Au	AuP	AuCl	PH	HPAu ($^\circ$)
MP2/2f	2f	232.9	244.1	141.7	119.0
MP2/3f2g	3f2g	221.2	223.1	141.4	117.5
CCSD(T)	2f	238.9	243.5	142.3	119.7
CCSD(T)	3f2g	225.3	226.0	142.0	117.8
PBE	2f	226.3	228.9	144.1	118.7
PBE	3f2g	225.1	226.6	144.1	118.9
TPSS	2f	226.9	229.3	142.8	118.5
TPSS	3f2g	225.7	227.2	142.8	118.6
B97D	2f	227.6	230.3	143.6	118.6
B97D	3f2g	226.2	228.1	143.7	118.8
PBE-D3	2f	226.2	228.9	144.1	118.6
PBE-D3	3f2g	224.9	226.6	144.1	118.8
TPSS-D3	2f	226.7	229.3	142.8	118.3
TPSS-D3	3f2g	225.5	227.2	142.8	118.5
B97D-D3	2f	226.8	230.6	143.6	118.3
B97D-D3	3f2g	225.5	228.3	143.6	118.5
M06L	2f	228.9	230.3	142.4	118.6
M06L	3f2g	227.9	229.3	142.4	118.7
M06	2f	231.6	229.8	142.7	118.3
M06	3f2g	230.5	228.9	142.7	118.3
M06HF	2f	216.1	230.3	140.7	116.1
M06HF	3f2g	215.1	229.3	140.8	116.3
M062X	2f	224.8	232.2	141.7	117.5
M062X	3f2g	223.0	231.1	141.8	117.7
M05	2f	232.5	231.6	143.3	118.3
M05	3f2g	231.6	230.5	143.3	118.3
M052X	2f	224.4	230.5	142.0	117.4
M052X	3f2g	223.0	229.6	142.1	117.5
PW91	2f	226.3	229.2	143.9	118.4
PW91	3f2g	225.3	228.1	143.9	118.5
CAM-B3LYP	2f	227.7	229.2	142.3	117.8
CAM-B3LYP	3f2g	226.6	228.3	142.3	117.9
LC- ω PBE	2f	224.2	226.1	142.3	117.8
LC- ω PBE	3f2g	223.8	225.8	142.1	117.7
$[\text{AuCl}(\text{PPh}_3)]$	Exp. [64]	224.2	228.9		
$[\text{AuCl}(\text{PMe}_3)]$	Exp. [65]	223.3	231.0		
$[\text{AuCl}(\text{PET}_3)]$	Exp. [66]	223.9	228.4		
$[\text{AuCl}(\text{PMe}_2\text{Ph})]$	Exp. [67]	223.6	231.6		

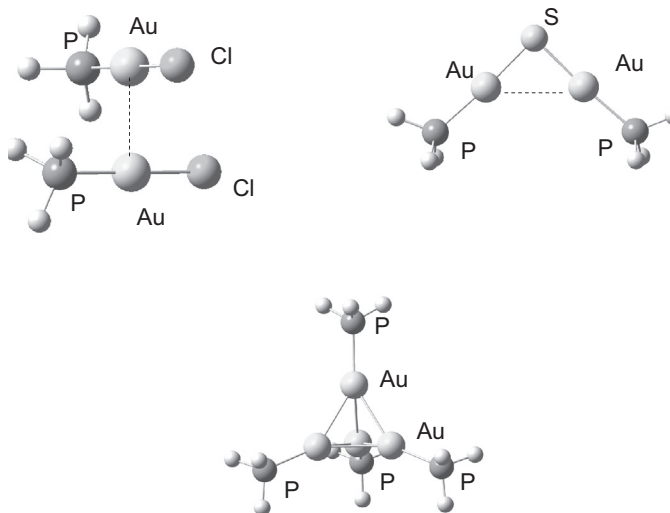


Fig. 1. Intermolecular interaction models of $[\text{AuCl}(\text{PH}_3)]_2$, $[\text{S}(\text{AuPH}_3)_2]$ and $[\text{AuPH}_3]_4^{2+}$.

0.40) [36]. The reason for using two basis sets is to compare the effect of the size of the base on the dispersion. It has already been shown that is necessary to use functions with diffusion and polarization to describe correctly the aurophilic interaction

[12–15]. The augmented correlation-consistent valence-triple-zeta (aug-cc-pVTZ) basis sets were used for S, P, Cl and H.

The Au–Au intermolecular interaction energy was obtained using each of the following post-Hartree–Fock methods: MP2, SCS-MP2 and CCSD(T), and the DFT functionals PBE, TPSS, B97; where Grimme dispersion correction was used for those functionals for which it is available, and its use is indicated by appending “DFT-D3” to the acronym of the density functional [49,50,63]. Moreover, M06L, M06, M06HF, M062X, M05, M052X, PW91, CAM-B3LYP and LC- ω PBE were used [47,48]. We have used the functional described above because they are the most common used in the study of the aurophilic interactions. The counterpoise correction for the basis-set superposition error (BSSE) was used for the calculated interaction energies.

3. Results and discussion

Table 1–5 summarizes the main geometric parameters and interaction energies obtained for the model systems at the different levels of theory of the calculations. In this section we will discuss the geometries and interaction energies for each system under study.

[ClAuPH₃]₂. The geometry of the monomer was fully optimized at several levels. A C_{3v} point symmetry was used. The optimized geometries are given in Table 1. For the post-Hartree–Fock (MP2 and CCSD(T)) calculations it was possible to see changes of the geometric parameters depending on which of the two bases was used for gold; in particular, the Au–P and Au–Cl were shortened. These

Table 2
Intermolecular distance Au–Au (pm) and interaction energy, $V(R_e)$, in kJ/mol for the [AuClPH₃]₂ model with counterpoise (CP) correction. Two basis sets on gold (2f and 3f2g).

System	Method	2f		3f2g	
		Au–Au	$V(R_e)$	Au–Au	$V(R_e)$
[AuClPH ₃] ₂	MP2	320.5	–24.9	304.4	–33.6
	SCS-MP2	334.9	–16.9	323.1	–20.8
	CCSD(T)	335.9	–15.4	327.9	–19.9
	PBE	345.8	–7.88	347.4	–7.51
	TPSS	348.5	–3.92	348.3	–4.09
	B97D	428.8	–1.25	436.4	–1.12
	PBE-D3	334.6	–27.9	334.2	–27.9
	TPSS-D3	329.9	–32.9	329.9	–34.2
	B97D-D3	331.8	–34.8	332.0	–35.1
	M06L	318.5	–24.6	319.9	–23.4
	M06	312.8	–27.9	314.9	–27.0
	M06HF	317.8	–23.8	320.2	–22.8
	M062X	326.5	–25.1	328.3	–24.1
	M05	346.0	–11.0	348.1	–10.8
	M052X	315.9	–26.1	317.5	–24.4
	PW91	322.6	–14.9	325.2	–14.1
	CAM-B3LYP	339.5	–7.30	343.6	–6.68
	LC- ω PBE	316.5	–22.4	316.8	–21.9
	MP2 [12]	320.8	–24.7		
	MP2 [14]	317.0	–25.5		
	MP2 [13]	326.0	–20.9		
	LMP2 [13]	333.0	–16.5		
	CCSD(T) [14]	336.0	–15.4		
	MP2 [36]			300.0	–37.0
	LMP2 [36]			303.0	–34.8
	BP86 [44]	319.0	–7.87		
BP86 [14]	326.0	–5.50			
LC- ω PPPE [52]	316.8	–23.4			
[AuCl(PPh ₃)] ₂	Exp. [64]	344.0			
[AuCl(PMe ₃)] ₂	Exp. [65]	333.8			
[AuCl(PEt ₃)] ₂	Exp. [66]	361.5			
[AuCl(PMe ₂ Ph)] ₂	Exp. [67]	323.0			

Table 3
Finite field calculations of electric properties of [ClAuPH₃]₂ monomer at the MP2 level. All values in a.u.

Properties	[ClAuPH ₃] ₂ ^a
μ	3.16377
α	70.52364
$\alpha_{ }$	103.53210
α_{\perp}	53.9825
θ	2.7327
IP ₁	0.3751

^a Gold atom with “2f” base set.

Table 4
Intramolecular Au–Au distance (pm) by the [S(AuPH₃)₂] model. Basis set on gold is 2f.

System	Method	Au–Au	S–Au	Au–P	AuSAu (°)
[S(AuPH ₃) ₂]	MP2	290.2	228.6	227.5	78.8
	SCS-MP2	296.6	229.8	226.4	80.3
	CCSD(T)	299.5	232.0	232.1	80.4
	PBE	321.6	230.3	226.3	88.8
	TPSS	310.4	230.9	226.9	88.5
	B97D	330.4	231.7	227.5	90.9
	PBE-D3	326.6	230.4	226.1	90.3
	TPSS-D3	326.4	230.9	226.5	89.9
	B97D-D3	336.0	232.1	226.5	92.7
	M06L	306.8	231.8	233.0	82.8
	M06	316.7	231.9	235.9	86.1
	M06HF	332.5	229.2	218.5	93.0
	M062X	333.7	231.8	228.6	92.1
	M05	320.4	232.6	236.2	87.0
	M052X	330.1	230.4	227.7	91.5
	PW91	317.5	230.8	229.9	86.9
	CAM-B3LYP	330.5	230.2	230.7	91.8
	LC- ω PBE	318.7	228.4	228.2	88.5
	MP2 [55]	291.4	228.2	227.3	79.4
	CCSD(T) [55]	303.0	231.3	232.1	81.8
	MP2 [45]	291.1	228.2	227.3	79.3
	MP4 [45]	292.1	230.6	230.3	78.6
	CCSD(T) [45]	303.0	231.3	232.1	81.6
	Xalpha [45]	299.0	226.2	222.0	82.9
	VWN [45]	298.0	225.5	221.0	82.7
	PB [45]	305.0	229.3	225.0	83.5
PW91 [45]	306.0	228.0	226.0	84.2	
MP2 [56]	291.4			79.4	
CCSD(T) [56]	301.8			82.8	
PBE [56]	321.0			89.4	
B3LYP [56]	337.0			95.2	
[S(AuPPh ₃) ₂]	Exp. [71]	301.8	215.9	213.5	88.7

values approach the experimental values [64–67] for the “3f2g” base. However, geometric parameters at the DFT level did not vary when we changed the basis set on gold.

The [ClAuPH₃]₂ dimer system has been widely studied by various groups during the past 25 years [12–14,39,40,44,51,52,68]. In order to compare and systemize the aurophilic intermolecular interaction, we have included the reported results in Table 2, where we summarize the interaction energies and Au–Au distances. For comparison we also included data from experimental structures. At the MP2, SCS-MP2 and CCSD(T) levels, results reported in this study are at the same level reported in the literature for both the interaction energy and the geometry. When we move from a 2f to a 3f2g basis for gold, the Au–Au interaction energy increases, while the Au–Au distance decreases. This is a clear effect of the aurophilic interaction. We are in the basis set limit. This coincides with the results obtained by Pyykkö and Zaleski-Ejgierd [69]. The only novelty in these results is the SCS-MP2 method, which generates results of similar accuracy to

Table 5
Intramolecular Au–Au distance (pm) by the $[\text{AuPH}_3]_2^+$ model. Basis set on gold is 2f.

System	Method	Au–Au	P–Au	P–H	Au–Au–Au (°)
$[\text{AuPH}_3]_2^+$	MP2	268.9	229.8	138.1	60
	SCS-MP2	272.1	231.9	138.2	60
	CCSD(T)	272.8	232.1	141.7	60
	PBE	277.8	232.4	140.5	60
	TPSS	275.6	233.6	139.1	60
	B97D	281.6	233.6	139.7	60
	PBE-D3	278.1	231.9	140.5	60
	TPSS-D3	276.0	232.7	139.1	60
	B97D-D3	285.1	231.9	139.6	60
	M06L	278.9	239.3	141.8	60
	M06	283.4	240.8	142.4	60
	M06HF	275.4	225.8	140.6	60
	M062X	284.4	236.5	141.5	60
	M05	287.9	241.4	143.0	60
	M052X	280.9	234.1	141.8	60
	PW91	277.1	235.6	143.4	60
	CAM-B3LYP	278.4	237.1	142.0	60
	LC- ω PBE	275.3	235.0	142.1	60
	MP2 [57]	271.8	246.0	143.0	
	TPSS [59]	276.3	234.2		
LC- ω PBE [59]	275.7	232.3			
CAM-B3LYP [59]	278.7	234.7			
$[\text{AuP}(\text{tBu})_3]_2^+(\text{BF}_4)_2$	Exp. [72]	271.4	230.5		59.7–60.4
$[\text{AuP}(\text{Mes})_3]_2^+(\text{BF}_4)_2$	Exp. [73]	273.4	235.5		59.7–60.4

tBu = tert-butyl.

Mes = mesityl.

CCSD(T), but at a lower computational expense. For small systems like AuH–Au₂, they have already been described by Pyykkö et al. [43].

When we analyze the results obtained by using DFT, regardless of the specific methods used, we notice that when going from a 2f to a 3f/2g basis there is virtually no change in the interaction energy and the Au–Au distance of the dimer. This clearly shows that for different DFT methods the aurophilic interaction is not sensitive to changes of basis set used for gold. For the PBE, TPSS and B97D functionals, only after the dispersion corrections (D3 corrections) were included, the interaction energy and Au–Au distances were comparable to those obtained at the MP2 level. These results with D3 corrections are similar to those obtained in the same dimer by Mata and Andrejic at the PBE and B3LYP levels [51].

For the second group of DFT functionals, the results obtained between M06L and LC- ω PBE showed strong oscillations, while for the M06L, M06, M06HF, M062X and M052X functionals the Au–Au interaction energies were in the same range as the MP2 result with the 2f basis, though the Au–Au equilibrium distances are shorter compared to MP2. On the other hand, the CAM-B3LYP and LC- ω PBE functionals give a poor description of the interaction energies. It should be noted that a study by Otero-de-la-Roza gives a better result for the same dimer [52]. We are able to reproduce their results with the LC- ω PBE functional. The best result is obtained with the PW91 functional, with which the interaction energy and the Au–Au equilibrium distance were at the same level as the results with SCS-MP2 and CCSD(T) methods. These results are supported by studies where the PW91 functional has been used to describe weak interactions in other systems with good results [70].

We are also interested in studying the effect of long-range behavior in the Au–Au interaction in order to compare the different methods. As reported by Pyykkö and Mendizabal [68], we have used the analytical expressions presented in Ref. [68]. We have included post-Hartree-Fock methods and DFT (PBE, TPSS, and B97D functionals) with and without dispersion correction (–D3).

The long-range behavior can be compared with the induction (ind) and the dispersion (disp) terms, which can be used to understand the predominant bonding mechanism. We have used Eqs. (1) and (2) to describe the terms involved in the limit of long distances for the dimer.

$$V_{\text{ind}} = - \left[\frac{\alpha \mu^2}{R^6} + \frac{1}{3} \frac{(\alpha_{\parallel} \alpha_{\perp})}{R^6} \mu^2 \right] \quad (1)$$

$$V_{\text{disp}} = - \frac{3}{4} \frac{\text{IP}_1}{R^6} \left[\alpha^2 - \frac{1}{3} \alpha(\alpha^{\parallel} - \alpha^{\perp}) \right] \quad (2)$$

Table 3 lists the electronic properties of the $[\text{ClAuPH}_3]$ monomer with the “2f” basis set. Figs. 2 and 3 show the curves for induction and dispersion terms from Eqs. (1) and (2) and the different methods used in the description of Au–Au interaction. In Fig. 2 we have used the results based on the “2f” basis set of the same methods. At short distances ranging between 300 and 400 pm it is possible to appreciate the differences in the methods discussed above. These differences are dominated by the repulsive and electronic correlation terms interaction. At long distances, the results can be divided between the post-Hartree-Fock and the DFT methods. The long-range behavior can be compared to the sum of the two R^{-6} induction and dispersion attractive terms estimated with Eqs. (1) and (2), respectively. This behavior is very similar to that obtained at the MP2 level in Ref. [68]. It is possible to estimate the contribution of these two forces at the Au–Au equilibrium distance of 320.5 pm at the MP2 level. The contribution of the induction term is 40% and that of the dispersion term is 60%. Both terms have a similar weight at short range. The DFT methods underestimate the interaction, but they keep the trend of R^{-6} . Fig. 3 shows the short- and long-range behavior, in which only the post-Hartree-Fock consider both basis sets on the gold. At long distance, all methods exhibit equal trend and magnitude.

[S(AuPH₃)₂]. The optimized structures for the A-frame molecule $[\text{S}(\text{AuPH}_3)_2]$ are shown in Table 4. We have used this molecule as a model to describe the intramolecular aurophilic interaction. The post-Hartree-Fock results based on the Au–Au distance and Au–S–Au angle are in close agreement with the experimental values used as Ref. [71] and to other theoretical results that have been published [54–56]. As seen in Table 4, MP2 overestimates the Au–Au and Au–S–Au stabilization reflected by the shorter distance and angle, while SCS-MP2 and CCSD(T) were very close to the crystal structure.

On the other hand, DFT results show an Au–Au distance and Au–S–Au angle greater than those obtained with the post-Hartree-Fock methods as described above. From the results based

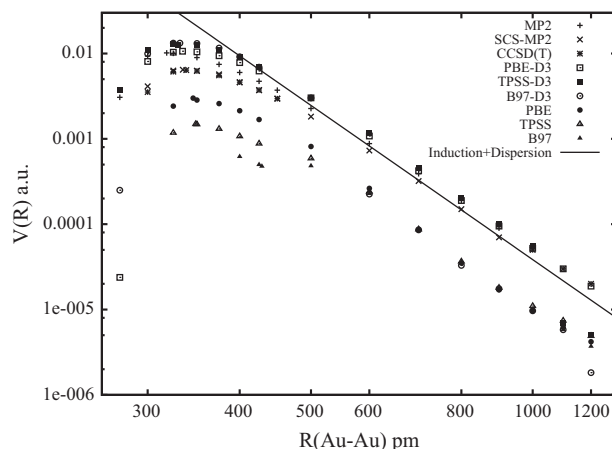


Fig. 2. Long-range limit in the $[\text{AuCl}(\text{PH}_3)_2]_2$ dimer at the post-Hartree-Fock and DFT levels.

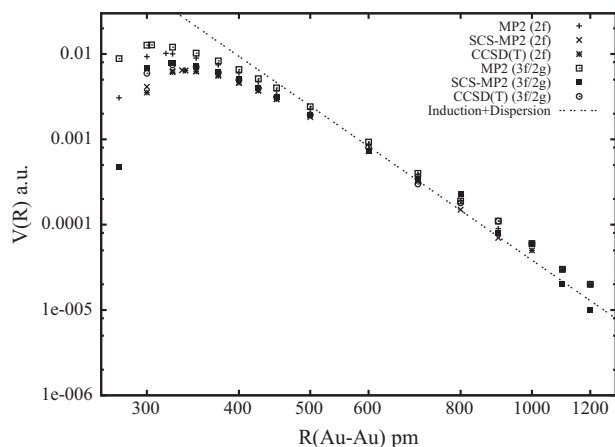


Fig. 3. Long-range limit in the $[\text{AuCl}(\text{PH}_3)_2]_2$ dimer at the post-Hartree–Fock levels with the basis on gold.

on DFT, we can highlight those obtained with M06L, M06, PW91 and LC- ω PBE, which provided an Au–Au distance closest to the experimental value (301.8 pm). The rest of the methods underestimated the reference distance (Au–Au). We also noticed that the DFT Grimme correction method (D3) was unable to decrease the Au–Au distance.

$[\text{AuPH}_3]_2^{2+}$. The geometry obtained at the MP2 level showed a Au–Au distance of 268.9 pm, very close to the 271.8 pm reported by Pyykkö and Runeberg [57]. As seen in Table 5, the difference occurs because we have fully optimized the geometry, while Pyykkö only optimized the distance between the Au atoms. However, the effect on the Au–Au bond is the same. The results at the SCS-MP2 and CCSD(T) levels are very similar and show a slightly longer Au–Au distance close to that of the experimental values [72,73].

All DFT calculations show a longer Au–Au distance compared to the post-Hartree–Fock. When Grimme correction was included no significant effect was noticed. The reported values are comparable to those obtained by Aikens et al. [59] with different DFT methods. Regardless of the method used, the rest of the geometric parameters such as P–Au, Au–PH and Au–Au–Au angle remained without significant changes.

4. Conclusions

We have focused the study of inter- and intramolecular aurophilic interaction by the classical models: $[\text{ClAuPH}_3]_2$, $[\text{S}(\text{AuPH}_3)_2]$ and $[\text{AuPH}_3]_2^{2+}$. As has been shown by various groups and by ourselves, the post-Hartree–Fock methods provide results in better agreement with the experimental values compared to DFT-based methods. Among the former it is possible to highlight the results obtained by the SCS-MP2 and CCSD(T) methods. At Au–Au equilibrium and long distances in the $[\text{ClAuPH}_3]_2$ dimer, the aurophilic interaction is driven by the induction and dispersion terms.

With respect to DFT-based methods, they depend on whether inter- or intramolecular interactions as well as gold cluster bonds are being studied. Thus, for the $[\text{ClAuPH}_3]_2$ system the best geometry and interaction energy results are obtained by using the PW91 functional. For –D3 Grimme's correction, M06HF, M06L, M06 M062X and M052X are in the same range of results as MP2. At Au–Au equilibrium and long distances, the interaction is driven by the induction and dispersion terms. In the A-frame $[\text{S}(\text{AuPH}_3)_2]$ it can be seen that better behavior is achieved for the geometric parameters when the methods are M06L, M06, PW91 and LC- ω PBE, while for $[\text{AuPH}_3]_2^{2+}$ cluster the best geometry corresponds

to PBE-D3, TPSS-D3, M06HF, M06L, PW91, CAM-B3LYP, and LC- ω PBE.

In general, we can classify the relative strength of the different methods such as: $\text{MP2} > \text{CCSD(T)} \approx \text{SCS-MP2}$ in post-Hartree–Fock. On the other hand, D3 Grimme correction, M06HF, M06L, M06 M062X, M052X, CAM-B3LYP and LC- ω PBE provided results of similar accuracy at the MP2 level.

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References

- [1] H. Schmidbaur, In Gold-Progress in Chemistry, Biochemistry and Technology, John Wiley & Sons, New York, 1999.
- [2] M.C. Gimeno, A. Laguna, in: C. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry 1, vol. 6, Elsevier, Amsterdam, 2004, pp. 911–1145.
- [3] H. Schmidbaur, A. Schier, A briefing on aurophilicity, Chem. Soc. Rev. 37 (2008) 1931–1951.
- [4] M.C. Gimeno, A. Laguna, Chalcogenide centred gold complexes, Chem. Soc. Rev. 37 (2008) 1952–1966.
- [5] A. Laguna (Ed.), Modern Supramolecular Gold Chemistry, Wiley-VCH, Weinheim, 2008.
- [6] X. Liu, J. Zhang, X. Guo, S. Wu, S. Wang, Gold nanoparticles for the colorimetric and fluorescent detection of ions and small organic molecules, Nanotechnology 21 (2010) 095501–095509.
- [7] H. Schmidbaur, A. Schier, Aurophilic interactions as a subject of current research: an up-date, Chem. Soc. Rev. 41 (2012) 370–412.
- [8] J.P. Fackler, Copper, gold and nickel clusters with and without metal-metal bonds in 50 years of Fackler group chemistry, Inorg. Chim. Acta 424 (2015) 83–90.
- [9] P. Pyykkö, Strong closed-shell interactions in inorganic chemistry, Chem. Rev. 97 (1997) 597–636.
- [10] P. Pyykkö, N. Runeberg, F. Mendizabal, Theory of the d10–d10 closed-shell attraction: 1. Dimers near equilibrium, Chem. Eur. J. 3 (1997) 1451–1457.
- [11] N. Runeberg, M. Schütz, H.-J. Werner, The aurophilic attraction as interpreted by local correlation methods, J. Chem. Phys. 110 (1999) 7210–7215.
- [12] P. Pyykkö, Theoretical chemistry of gold, Angew. Chem. Int. Ed. 43 (2004) 4412–4456.
- [13] E. ÓGrady, N. Kaltsoyannis, Does metallophilicity increase or decrease down group 11? Computational investigations of $[\text{Cl-M-PH}_3]_2$ (M = Cu, Ag, Au, [111]), Phys. Chem. Chem. Phys. 6 (2004) 680–687.
- [14] M. Dolg, P. Pyykkö, N. Runeberg, Calculated structure and optical properties of $\text{Ti}_2\text{Pt}(\text{CN})_4$, Inorg. Chem. 35 (1996) 7450–7451.
- [15] P. Pyykkö, Theoretical chemistry of gold III, Chem. Soc. Rev. 37 (2008) 1967–1997.
- [16] E.J. Fernández, P.G. Jones, P.G.A. Laguna, J.M. López-de-Luzuriaga, F. Mendizabal, M. Monge, M.E. Olmos, M. Pérez, Theoretical and photoluminescence studies on the $d^{10}\text{-s}^2$ $\text{Au}^{\text{I}}\text{-Ti}^{\text{I}}$ interaction in extended unsupported chains, Chem. Eur. J. 9 (2003) 456–465.
- [17] E.J. Fernández, J.M. López-de-Luzuriaga, M. Monge, Montiel, M.E. Olmos, J. Pérez, A. Laguna, F. Mendizabal, A.A. Mohamed, J.P. Fackler, A detailed study of the vapochromic behavior of $[\text{Ti}[\text{Au}(\text{C}_6\text{Cl}_5)_2]_n]$, Inorg. Chem. 43 (2004) 3573–3581.
- [18] F. Mendizabal, P. Pyykkö, Aurophilic attraction in binuclear complexes with Au(I) and Au(III). A theoretical study, Phys. Chem. Chem. Phys. 4 (2004) 900–905.
- [19] F. Mendizabal, G. Zapata-Torres, C. Olea-Azar, Theoretical study of the interaction $d^{10}\text{-s}^2$ between Pt(0) and Ti(I) on the $[\text{Pt}(\text{PH}_3)_3\text{Ti}]^+$ complex, Chem. Phys. Lett. 412 (2005) 477–481.
- [20] G. Tárkányi, P. Király, G. Pálkás, A. Deák, Conformational analysis of a helically distorted gold(I) macrocycle derived from xantphos: evidence for the aurophilic Au–Au interaction from NMR, Magn. Reson. Chem. 45 (2007) 917–924.
- [21] A. Deák, T. Megyes, G. Tárkányi, P. Király, L. Biczkó, G. Pálkás, P.J. Stang, Synthesis and solution- and solid-state characterization of gold(I) rings with short Au–Au interactions. Spontaneous resolution of a gold(I) complex, J. Am. Chem. Soc. 128 (2006) 12668–12670.
- [22] M. Haruta, Catalysis: gold rush, Nature 437 (2005) 1098–1099.
- [23] R.S. Paton, F. Maseras, Gold (I)-catalyzed intermolecular hydroalkoxylation of allenes: a DFT study, Org. Lett. 11 (2009) 2237–2240.
- [24] T. Ishida, M. Haruta, Oxygen-mediated coupling of alcohols over nanoporous gold catalysts at ambient pressures, Angew. Chem. Int. Ed. 119 (2007) 7288–7290.
- [25] D.W. Goodman, Precious little catalyst, Nature 454 (2008) 948–949.
- [26] A. Corma, H. Garcia, Supported gold nanoparticles as catalysts for organic reactions, Chem. Soc. Rev. 37 (2008) 2096–2126.
- [27] O. Vaughan, Crystal growth: curved single crystals of gold, Nat. Nanotechnol. 5 (2010) 5–15.

- [28] Y. Pei, X.C. Zeng, Investigating the structural evolution of thiolate protected gold clusters from first-principles, *Nanoscale* 4 (2012) 4054–4072.
- [29] S. Miranda-Rojas, A. Muñoz-Castro, R. Arratia-Pérez, F. Mendizabal, Theoretical insights into the adsorption of neutral, radical and anionic thiophenols on gold (111), *Phys. Chem. Chem. Phys.* 15 (2013) 20363–20370.
- [30] D.M. Chevrier, X. Meng, Q. Tang, D. Jiang, M. Zhu, A. Chatt, P. Zhang, Impact of the selenolate ligand on the bonding behavior of Au₂₅ nanoclusters, *J. Phys. Chem. C* 118 (2014) 21730–21737.
- [31] W.J. Hunks, M.C. Jennings, R.J. Puddephatt, Supramolecular gold (I) thiobarbiturate chemistry: combining aurophilicity and hydrogen bonding to make polymers, sheets, and networks, *Inorg. Chem.* 41 (2002) 4590–4598.
- [32] A. Codina, E.J. Fernandez, P.G. Jones, A. Laguna, M.J. Lopez-de-Luzuriaga, M. Monge, M.E. Olmos, J. Perez, M.A. Rodriguez, Do aurophilic interactions compete against hydrogen bonds? experimental evidence and rationalization based on ab initio calculations, *J. Am. Chem. Soc.* 124 (2002) 6781–6787.
- [33] F. Mendizabal, P. Pyykkö, N. Runeberg, Aurophilic attraction: the additivity and the combination with hydrogen bonds, *Chem. Phys. Lett.* 370 (2003) 733–740.
- [34] I.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin, X.-M. Chen, Metallophilicity versus π - π interactions: ligand-unsupported argentophilicity/cuprophilicity in oligomers-of-dimers [M₂L₂]_n (M = Cu or Ag, L = tridentate ligand), *Chem. Eur. J.* 11 (2005) 552–556.
- [35] F. Mendizabal, D. Reyes, C. Olea-Azar, Complexes self-associate by hydrogen bonding and metallophilic attraction: theoretical study, *Int. J. Quantum Chem.* 106 (2006) 906–912.
- [36] L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, H.-J. Werner, A comparison of metallophilic attraction in (X-M-PH₃)₂ (M = Cu, Ag, Au; X = H, Cl), *Phys. Chem. Chem. Phys.* 4 (2002) 1006–1013.
- [37] R.-F. Liu, C.A. Franzese, R. Malek, P.S. Zschowski, J.G. Angyan, M.M. Szczesniak, G. Chalasinski, Aurophilic interactions from wave function, symmetry-adapted perturbation theory, and range hybrid approaches, *J. Chem. Theory Comp.* 7 (2007) 2399–2407.
- [38] J. Muniz, C. Wang, P. Pyykkö, Aurophilicity: the effect of the neutral ligand L on [(ClAuL)₂] systems, *Chem. Eur. J.* 17 (2011) 368–377.
- [39] P. Pyykkö, Y.-F. Zhao, Ab initio calculations on the (ClAuPH₃)₂ dimer with relativistic pseudopotential: is the “aurophilic attraction” a correlation effect? (pages 604–605), *Angew. Chem. Int. Ed.* 30 (1991) 604–605.
- [40] P. Pyykkö, J. Li, N. Runeberg, Predicted ligand dependence of the Au(I)···Au(I) attraction in (XAuPH₃)₂, *Chem. Phys. Lett.* 218 (1994) 133–138.
- [41] S. Grimme, Improved second-order Møller–Plesset perturbation theory by separate scaling of parallel- and antiparallel-spin pair correlation energies, *J. Chem. Phys.* 118 (2003) 9095.
- [42] M. Gernkamp, S. Grimme, Spin-component scaled second-order Møller–Plesset perturbation theory for the calculation of molecular geometries and harmonic vibrational frequencies, *Chem. Phys. Lett.* 392 (2004) 229–235.
- [43] P. Pyykkö, X.-G. Xiong, J. Li, Aurophilic attractions between a closed-shell molecule and a gold clusters, *Faraday Discuss.* 152 (2011) 169–178.
- [44] S.-G. Wang, W.H.E. Schwarz, Quasi-relativistic density functional study of aurophilic interactions, *J. Am. Chem. Soc.* 126 (2004) 1266–1276.
- [45] H. Fang, S.-G. Wang, X.-G. Zhang, Density functional study of aurophilic interaction in Cl(AuPH₃)₂ and in its dimerization, *Int. J. Quantum Chem.* 109 (2009) 526–533.
- [46] H. Fang, X.-G. Zhang, S.-G. Wang, Density functional studies of closed-shell attractions of S(AuPH₃)₂ and HS(AuPH₃)₂ and their dimers, *J. Mol. Model.* 15 (2009) 461–468.
- [47] Y. Zhao, N.E. Schultz, D.G. Truhlar, Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions, *J. Chem. Theory Comput.* 2 (2006) 364–382.
- [48] Y. Zhao, D.G. Truhlar, Density functionals with broad applicability in chemistry, *Theor. Chem. Acc.* 120 (2008) 215–241.
- [49] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (2006) 1787–1799.
- [50] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction DFT-D for the 94 elements H–Pu, *J. Chem. Phys.* 132 (2010) 154104.
- [51] M. Andrejic, R.A. Mata, Study of ligand effects in aurophilic interactions using local correlation methods, *Phys. Chem. Chem. Phys.* 15 (2013) 18115–18122.
- [52] A. Otero-de-la-Roza, J.D. Mallory, E.R. Johnson, Metallophilic interactions from dispersion-corrected density-functional theory, *J. Chem. Phys.* 140 (2014) 18A504.
- [53] P. Pyykkö, Theoretical chemistry of gold II, *Inorg. Chim. Acta* 358 (2005) 4113–4130.
- [54] P. Pyykkö, T. Tamm, Theory of the d10–d10 closed-shell attraction. 4. X(AuL)_nm+ centered systems, *Organometallics* 17 (1998) 4842–4852.
- [55] S. Riedel, P. Pyykkö, R.A. Mata, H.-J. Werner, Comparative calculations for the A-frame molecules [S(MPH₃)₂] (M = Cu, Ag, Au) at levels up to CCSD(T), *Chem. Phys. Lett.* 405 (2005) 148–152.
- [56] M.M. Alam, E. Fromager, Metallophilic interactions in A-frame molecules [S(MPH₃)₂] (M = Cu, Ag, Au) from range-separated density-functional perturbation theory, *Chem. Phys. Lett.* 554 (2012) 37–42.
- [57] P. Pyykkö, N. Runeberg, Calculated properties of the ‘empty’ [AuPH₃]₄+2 and related systems: role of covalent and correlation contributions, *Chem. Commun.* (1993) 1812–1813.
- [58] M.J. Calhorda, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J.M. Lopez-de-Luzuriaga, J.L. Perez, M.A. Ramon, L.F. Veiros, Synthesis, structure, luminescence, and theoretical studies of tetranuclear gold clusters with phosphinocarborane ligands, *Inorg. Chem.* 39 (2000) 4280–4285.
- [59] S.A. Ivanov, I. Arachchige, C.M. Aikens, Density functional analysis of geometries and electronic structures of gold-phosphine clusters. The case of Au₄(PR₃)₄+2 and Au₄(μ₂-I)₂(PR₃)₄, *J. Phys. Chem. A* 115 (2011) 8017–8031.
- [60] Turbomole: ab initio program R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Electronic structure calculations on workstation computers: the program system turbomole, *Chem. Phys. Lett.* 162 (1989) 165–169.
- [61] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, K.T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 09 Inc, Pittsburgh PA, 2003.
- [62] (a) D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Energy-adjusted ab initio pseudopotentials for the second and third row transition elements, *Theor. Chim. Acta* 77 (1990) 12–25; (b) T. Leininger, A. Berning, A. Nicklass, H. Stoll, H.J. Wener, H.J. Flad, Spin-orbit interaction in heavy group 13 atoms and TIAr, *Chem. Phys.* 217 (1997) 19–27.
- [63] W. Hujo, S. Grimme, Performance of the van der Waals density functional VV10 and (hybrid) GGA variants for thermochemistry and noncovalent interactions, *J. Chem. Theory Comput.* 7 (2011) 3866–3871.
- [64] H. Schmidbaur, G. Weidenhiller, O. Steigelmann, G. Müller, Triaurierte phosphonium-ionen [RP(AuPPh₃)₃] und das elektronendefizitäre, hyperkoordinierte phosphonium-dikation [P(AuPPh₃)₅], *Chem. Ber.* 123 (1990) 285–287.
- [65] K. Angermaier, E. Zeller, H. Schmidbaur, Crystal structures of chloro (trimethylphosphine) gold (I), chloro (tri-propylphosphine) gold(I) and bis (trimethylphosphine) gold(I) chloride, *J. Organometallic Chem.* 472 (1994) 371–376.
- [66] E.R.T. Tiekink, Chloro(triethylphosphine)gold(I), *Acta Crystallogr.* C45 (1989) 1233–1242.
- [67] K. Angermair, G.A. Bowmaker, E.N. de Silva, P.C. Healy, B.E. Jones, H. Schmidbaur, Vibrational and solid-state phosphorus-31 nuclear magnetic resonance spectroscopic studies of 1:1 complexes of PPh₃ with gold(I) halides; crystal structure of [AuBr(PMe₃)₃], *J. Chem. Soc. Dalton Trans.* (1996) 3121–3129.
- [68] P. Pyykkö, F. Mendizabal, Theory of the d10–d10 closed-shell attraction: 2. long-distance behaviour and nonadditive effects in dimers and trimers of type [(x-Au-L)_n] (n = 2, 3; X = Cl, I, H; L = PH₃, PMe₃, -N≡CH), *Chem. Eur. J.* 3 (1997) 1458–1465.
- [69] P. Pyykkö, P. Zaleski-Ejgierd, Basis-set limit of the aurophilic attraction using the MP2 method: the examples of [ClAuPH₃]₂ dimer and [P(AuPH₃)₄]⁺ ion, *J. Chem. Phys.* 128 (2008) 124309.
- [70] E.R. Johnson, G.A. DiLabio, Structure and binding energies in van der Waals dimers: comparison between density functional theory and correlated ab initio methods, *Chem. Phys. Lett.* 419 (2006) 333–339.
- [71] C. Lensch, P.G. Jones, G.M. Sheldrick, Kristallstrukturen der selenid-bzw. sulfidverbrückten Gold(I)verbindungen [Se(AuPPh₃)₃]PF₆⁻ und [S(AuPPh₃)₂]CH₂C1₂, *Z. Naturforsch. B* 37 (1982) 944–946.
- [72] E. Zeller, H. Beruda, H. Schmidbaur, Tetrahedral gold cluster [Au₄]²⁺: crystal structure of [(tBu)₃PAuH]₂+(BF₄)₂CHCl, *Inorg. Chem.* 32 (1993) 3203–3204.
- [73] Y. Yang, R. Sharp, Gold(I) heteroatom-substituted imido complexes. amino nitrene loss from [(LAU)₃(μ-NNR₂)]⁺, *J. Am. Chem. Soc.* 116 (1994) 6983–6984.