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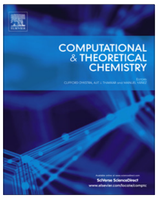

A comparative study between post-Hartree–Fock methods and density functional theory in closed-shell aurophilic attraction

Fernando Mendizabal [a,*], Sebastián Miranda-Rojas [b], Lorena Barrientos-Poblete [c]

[a] Departamento de Química, Facultad de Ciencias, Universidad de Chile, P.O. Box 653, Las Palmeras 3425, Ñuñoa, Santiago, Chile
[b] Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, Avenida República 275, Santiago, Chile
[c] Departamento de Química, Facultad de Ciencias Básicas, Universidad Metropolitana de Ciencias de la Educación, Casilla 147, Santiago, Chile

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ABSTRACT

The inter- and intramolecular aurophilic $[ClAuPH_3]_2$, $[S(AuPH_3)_2]$ and $[AuPH_3]_4^{2+}$ 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 $[ClAuPH_3]_2$ 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-ωPBE provided results of similar accuracy as MP2.

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 mettaphilic 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-Hertee–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 a accurate and efficient tool for incorporating electronic correlation to the study of large systems.

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[*] Corresponding author.

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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 $[ClAuPH_3]_2$ 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, $(AuH)_2$ and $(HAuPH_3)_2$ systems [37]. Finally, the LC-ωPBE-XDM method has been implemented to study interactions in simple aurophilic dimers $[XAuPH_3]_2$ (X = H, Cl, Br, 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 $[S(AuPH_3)_2]$ and $[AuPH_3]_4^{2+}$, 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, $[AuPH_3]_4^{2+}$, 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 $[AuPH_3]_4^{2+}$ 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: $[ClAuPH_3]_2$, $[S(AuPH_3)_2]$ and $[AuPH_3]_4^{2+}$. 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 $[ClAuPH_3]$ monomer at the different theory levels (see Table 1). Then, we used this geometry to study the Au–Au intermolecular interactions in the $[ClAuPH_3]_2$ dimer (see Fig. 1) with C_2 symmetry (with a 90° dihedral angle) [12]. The $[S(AuPH_3)_2]$ (C_{2v}) and $[AuPH_3]_4^{2+}$ (C_{3v}) models describe the intramolecular Au–Au interaction and the gold bonds in a small cluster, respectively.

Table 1
Main geometric parameters of the $[AuCl(PH_3)]$ monomer model studied. Distances in pm and angles in degrees.

Method	Basis on Au	AuP	AuCl	PH	HPAu (°)
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-ωPBE	*2f*	224.2	226.1	142.3	117.8
LC-ωPBE	*3f2g*	223.8	225.8	142.1	117.7
$[AuCl(PPh_3)]$	Exp. [64]	224.2	228.9		
$[AuCl(PMe_3)]$	Exp. [65]	223.3	231.0		
$[AuCl(PEt_3)]$	Exp. [66]	223.9	228.4		
$[AuCl(PMe_2Ph)]$	Exp. [67]	223.6	231.6		

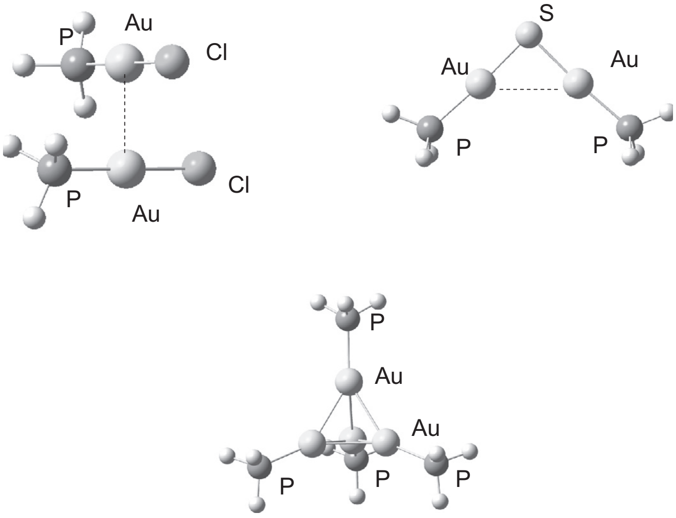

Fig. 1. Intermolecular interaction models of $[AuCl(PH_3)]_2$, $[S(AuPH_3)_2]$ and $[AuPH_3]_4^{2+}$.

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 ($\alpha_f = 1.41, 0.40, 0.15$; $\alpha_g = 1.20, 0.40$) [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