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

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The inter- and intramolecular aurophilic [ClAuPH3]2−, [S/AuPH3]2−, and [AuPH3]4− 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 [ClAuPH3]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, M06H, M06L, M06 M062X, M052X, CAM-B3LYP and LC-ωPBE provided results of similar accuracy as MP2.

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1. Introduction

It is well established that the attractive interactions between cations with d8, d10 and s2 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 ŐGrady and Kaltsbayannis 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 metaphilic 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 characterististics 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 a accurate and efficient tool for incorporating electronic correlation to the study of large systems.
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 changing in recent years due to several attempts to incorporate a dispersion term by different means. 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2. Computational details

First we fully optimized the geometry of the [ClAuPH₃]⁺ monomer at the different theory levels (see Table 1). Then, we used this geometry to study the Au–Au intermolecular interactions in the [ClAuPH₃]⁺ dimer (see Fig. 1) with C₂ symmetry (with a 90° dihedral angle) [12]. The [S(AuPH₃)₂]⁺ (C₂v) and [AuPH₃]⁺²⁺ (C₂v) 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 (V2ZP); two f-type (2f) polarization functions were added to Au (ṣ₂ = 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 (ṣ₂ = 1.41, 0.40, 0.15;  ᵙ₂ = 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 it is necessary to use functions with diffusion and polarization to describe correctly the aurophilic interaction.
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-oPBE 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 C3v point symmetry was used. The optimized structures 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 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 Pykkö and Zaleski-Ejgierd [69]. The only novelty in these results is the SCS-MP2 method, which generates results of similar accuracy to

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>(2f) Au–Au ((R_a))</th>
<th>(3f2g) Au–Au ((R_a))</th>
<th>(3f2g) S–Au ((R_a))</th>
<th>(3f2g) Au–P ((R_a))</th>
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<td>[AuCl(PPh3)]2</td>
<td>Exp. [64]</td>
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<td>7.87</td>
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<td>[AuCl(PMe2Ph)]2</td>
<td>Exp. [65]</td>
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<td>5.50</td>
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<td>[AuCl(PMePh)]2</td>
<td>Exp. [66]</td>
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<td>3.92</td>
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<tr>
<td>[AuCl(PMePh)]2</td>
<td>Exp. [67]</td>
<td>323.0</td>
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</tr>
</tbody>
</table>

Table 3

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

| \(\mu\) | 3.16377 |
| \(\alpha\) | 70.52364 |
| \(\beta\) | 103.53210 |
| \(\gamma\) | 54.9825 |
| \(\delta\) | 2.7327 |
| \(\Omega\) | 0.3751 |

Table 4

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

Property | Method | \(\mu\) | \(\alpha\) | \(\beta\) | \(\gamma\) | \(\delta\) | \(\Omega\) |
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<td>(\mu)</td>
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<td>(\alpha)</td>
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<td>(\gamma)</td>
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<td>(\delta)</td>
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<td>(\Omega)</td>
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</table>
their results with the LC-ω x included post-Hartree-Fock methods and DFT (PBE, TPSS, and B97D). Mes = mesityl.

Intramolecular Au–Au distance (pm) by the [AuPH3]4
dimer. 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.

\[
V_{\text{ind}} = \frac{1}{a^2} \left( \frac{2}{3} \chi \delta - \frac{2}{3} \chi \delta \right)
\]

\[
V_{\text{disp}} = \frac{3 \chi a}{R^6} \left( 2 - \frac{1}{3} \chi \delta \right)
\]

Table 3 lists the electron properties of the [ClAuPH3]4 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.

\[
[S(AuPH3)]4
\]

monomer. The optimized structures for the A-frame molecule \([S(AuPH3)]4\) 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

**Table 5**

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

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Au–Au</th>
<th>P–Au</th>
<th>P–H</th>
<th>Au–Au–Au (°)</th>
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<tr>
<td>[AuPH3]4</td>
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<td>231.9</td>
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<td>CCSD(T)</td>
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<td>232.1</td>
<td>141.7</td>
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<td>TPSS</td>
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<td>233.6</td>
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<td>60</td>
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\[^{1}\text{Bu} = \text{tert-butyl.}

\[^{2}\text{Mes} = \text{mesityl.}

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.

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\]

\[
V_{\text{disp}} = \frac{3 \chi a}{R^6} \left( 2 - \frac{1}{3} \chi \delta \right)
\]

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 3f2g 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-oPBE 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-oPBE 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-oPBE 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).
on DFT, we can highlight those obtained with M06L, M06, PW91 and LC-oPBE, 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.

**[AuPh3]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 Runemberg. 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 angle remained without significant changes.

### 4. Conclusions

We have focused the study of inter- and intramolecular aurophilic interaction by the classical models: [ClAuPh3]2+, [SAuPh3]2+ and [AuPh3]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 [ClAuPh3]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 [ClAuPh3]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 [SAuPh3]2+ it can be seen that better behavior is achieved for the geometric parameters when the methods are M06L, M06, PW91 and LC-oPBE, while for [AuPh3]2+ cluster the best geometry corresponds to PBE-D3, TPSS-D3, M06HF, M06L, PW91, CAM-B3LYP, and LC-oPBE.

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

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### References

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