

Quasi-Relativistic Density Functional Study of Auophilic Interactions

Shu-Guang Wang and W. H. Eugen Schwarz*

Contribution from the Theoretical Chemistry Group, Department of Chemistry, School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 200 240 Shanghai, China; and Theoretical Chemistry, Chemistry Department, University Siegen, D-57068 Siegen, Germany

Received March 11, 2003; E-mail: schwarz@chemie.uni-siegen.de

Abstract: Fifteen molecules containing the Au(I) species have been calculated by ab initio HF and MP2 methods and by five different density functional approaches. The auophilic Au(d^{10})–Au(d^{10}) bonding mechanism has been investigated. Both, one-electron interactions (i.e., electrostatic, polarization, charge transfer, and orbital interference) and two-electron effects (i.e., correlation, dispersion) contribute significantly to the so-called ‘secondary’ or metallophilic bonds representing the Au–Au interaction. Second, the applicability of density functional approaches to this type of bonding has been tested. It is well-known that present day density functionals are not yet designed to simulate the long-range London dispersion forces between nonoverlapping systems, whereas they approximately reproduce the short range dynamical electron correlations of strongly overlapping chemically bonded nondegenerate species. It is found here empirically for the investigated groups of gold(I) cluster compounds that simple local density functionals (LDF) of the Slater (or Slater plus Vosko) type yield rather reasonable estimates for the equilibrium distances, and (on the average) also for the auophilic interaction energies, though with rather large standard deviations. Still LDF are useful for survey investigations of Au cluster compounds. Common gradient corrected DF are not recommended here, nor are the large core pseudopotentials for Au.

Introduction

1.1 Auophilicity. It is now well-known that the very specific properties of gold are determined to a significant extent by the strong relativistic modifications of its 5d and 6s valence shells.^{1–6} One common and rather specific property of monovalent gold compounds is their tendency to form clusters of Au(I) species. This is now commonly attributed to unusually strong d^{10} – d^{10} interactions,^{2–5,7–12} although ligand interactions and packing effects may also play a role, e.g.^{13–16}

In many gold(I) compounds, the Au atom is diagonally coordinated in the first sphere, with linear or nearly linear

structure, $L \rightarrow Au-X$. In neutral gold(I) molecules, the formal Au^+ species is typically combined with more or less basic anions (e.g., halides X^- or nitrate NO_3^- or organic carbanions R^-) and/or with neutral electron donor ligands L (such as the phosphines or amines), preferably electronically soft ones. If X and L are not both too bulky, then the Au(I) complexes can become associated into Au(I)–Au(I) bonded clusters.

Au(I) species with closed d^{10} shells and with some positive partial charges on the Au (e.g., charges of about $+1/2$ on Au were mentioned in ref 94) might be expected to repel each other. The search for $Cu^+–Cu^+$ attractions had been unsuccessful for a long time.^{7,17–19} However, more recently evidence of d^{10} – d^{10} attractions of different types is accumulating, though becoming weaker from $Au^+–Au^+$ to $Ag^+–Ag^+$ to $Cu^+–Cu^+$.^{17,41,105} On the contrary, obviously bonded Au(I) cluster

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compounds are already known for a long time.²⁰ Detailed empirical studies have yielded typical contact distances of the order of $3 \pm \text{Å}$, with the smaller separations for electronically

soft ligands.³⁹ The interaction is associated with stabilization energies of 20 up to 50 kJ/mol.^{2–5,21,24,87–89,105} This is in the range of strong-hydrogen to weak-covalent bond energies. Accordingly, this type of interaction is more easy to study for Au than for Cu or Ag. Schmidbaur and co-workers have introduced the phrase “auophilic attraction” in 1988²² to name such kinds of interactions, which have become an interesting topic as another kind of ‘secondary bonds’ between the stronger ‘ordinary’ chemical bonds and the weaker van der Waals interactions. The intermediate metallophilic bonding (a phrase first suggested by Pyykkö et al.)³⁹ now forms an important tool in supramolecular, nanochemical and crystal engineering and in the manipulation of luminescence properties.^{23–27,30,48,92} Gold clusters and gold tips, bonded to sulfur or oxygen or halogen containing ligands, are an important topic.^{111,112}

The auophilicity phenomenon has been the subject of many theoretical treatments. When investigating the Pt(0)–Pt(0), Cu(I)–Cu(I), Au(I)–Au(I), Tl(I)–Tl(I), and In(I)–In(I) interactions at the simple *semiempirical one-electron level* of extended Hückel–molecular orbital (EH–MO) theory, Hoffmann, Burdett, Bénard and other scholars revealed an **orbital mixing** of

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nd and $(n+1)s,p$ based HOMO and LUMO (highest occupied and lowest unoccupied MO) interactions and/or more or less long ranging Coulomb attractions as the dominant mechanisms for such bonding interactions.^{8–10,28–33}

On the other hand, Pyykkö and other researchers^{2,34–42,63,91} have more recently carried out calculations at the ab initio independent particle *Hartree–Fock* self-consistent field (HF-SCF) level and at different more sophisticated, *electron-correlated levels*, starting with 2nd order Møller–Plesset (MP2) perturbation theory. At the HF-MO-SCF level no attraction at all between the Au(I) species was found, whereas significant Au(I)–Au(I) interaction energies were obtained at the different correlated levels. In particular, the weak attraction at larger distances follows an R^{-6} law (while at shorter distances also exponentially increasing correlations play a role¹⁰⁵). From these results, it was concluded that aurophilicity is a genuine **correlation-dispersion** effect, enhanced by induction and, in particular, by relativistic corrections, which may all be quite strong in heavy atomic systems.

DFT (Density Functional Theory) studies of aurophilic and general metallophilic interactions have also been reported, among others in refs 16, 33, 43–46, 99, 102, 107, and 108. The importance of Au 5d-6s-6p hybridization in those investigations has been pointed out.⁴⁵ The DF approach aims at representing the many particle correlation effects within the effective independent particle–MO picture. However, most DF approaches still have problems concerning the dispersion interactions of R^{-6} type between weakly- or nonoverlapping systems at larger distances. Significant failures of DFT for the lighter rare gas van der Waals systems have been reported,^{113,114} but it was found that the simple Slater type DF is comparatively close to experiment for the heavier Ar₂ system. It had already been found earlier⁶⁹ that simple local DF and ab initio MP2 approaches reproduce the experimental data on heavy systems such as Au₂ and Hg₂ better than the Hartree–Fock approximation, gradient corrected DF ones or their hybrids. DFT is usually not too bad concerning dynamical electron correlations between strongly overlapping systems without near-degeneracy perturbations. In recent years, different common versions of the DF approach have yielded quite different results for bond lengths and bond energies of Au(I) cluster systems. Therefore, the application of DFT to the problem of aurophilicity has undergone some general criticism.^{2,47}

Concerning the *relativistic corrections*, they are less critical. The *one-electron* dynamics and the resulting density distributions are known to be quite significant in gold compounds.¹ However, they can be approximated quite reliably at different levels of theory such as DPT (Direct Dirac Perturbation Theory) or RA (Regular Approximation) or REC (Relativistic Effective Core pseudopotential approximation, which was applied here). We note that the common *nonrelativistic two-electron* exchange-correlation functionals seem to be sufficient for the compounds of present interest.⁴⁴

1.2 Outline. The aim of the present study is 2-fold. Different DF perform with different reliabilities and different error trends for different classes of compounds and for different properties. On one hand, we will investigate empirically, which DF approaches, if any, give reasonable results for systems with

aurophilic interactions, concerning both the geometric structures and the aurophilic binding energies.

Second, we will study, for several different groups of aurophilic compounds, the individual importance and the interplay of *orbital interactions* (e.g., resulting in specific hybridization and in covalent or polycentric bonding), of *dispersion interactions* (i.e., electron correlation) and of *electrostatic interactions* (Coulomb attractions between the polar charge distributions on the gold and ligand atoms), all at the quasi-relativistic level.

The calculational details are described in section 2. Different series of aurophilic systems are calculated and discussed in section 3. More than 20 years ago, Lauher and Wald,¹¹⁵ and Hoffmann,²⁹ and later others^{14,48} pointed out that L–Au⁺ cations (where L is a nucleophilic ligand) can be classified as isolobal with carbocations R⁺, or even with H⁺, forming series of compounds such as O(AuL)₂, O(AuL)₃⁺, O(AuL)₄²⁺, and so on. We have chosen several series of respective Au(I) compounds for the present investigation.

A first series is EAu_n, where E is an *n*-valent atom or ion. For *n* = 2 we take E = Se; for *n* = 3: E = O⁺ or S⁺; and for *n* = 4: E = N⁺. In these compounds, the Au–E–Au bond angles form a sensitive probe of the Au–Au interactions. A related series investigated here is E(AuL)_n, where the electron pair donating ligand L reduces the effective charge on the Au atoms and thereby reduces their electrostatic repulsions and possibly induces some Au–Au covalence. Both these series are discussed in section 3.2. If E is monovalent (E = Cl with *n* = 1), then the respective compounds EAuL form Au^{δ±}–Au^{δ±} bonded dimers (section 3.1). To investigate the interaction of partially charged gold atoms and the influence of orbital interactions further, we have chosen the series (Au, AuL)₄^{q+} with *q* between –2 and +4, in section 3.3.

As a computationally simple prototype ligand we have chosen phosphine, L = PH₃. We admit that typical organic phosphine ligands PR₃ (especially if R is an aryl group) behave somewhat different from the parent molecule PH₃ concerning orbital and bonding energies, whereas the geometric structures are in general reproduced quite reasonably.^{38,43,45,49,50}

Finally, a summarizing and concluding discussion is presented in section 4. Our main answers are, in short, the following: First, Slater's simple X α potential (and to a lesser extent Vosko's "improved" local DF [LDF]) seems to produce reliable aurophilic structures. Slater's LDF also seems to yield rough estimates of binding energies for the aurophilic interaction. Second, the aurophilic interaction turns out to be a cooperative result of significant electric attractions, of rather small closed shell and charge repulsions, and of covalent *and* dispersion attractions, acting between the rather 'soft' and ligand-modified Au(I) species. We predict the existence of some new cluster types. We suggest that standard molecular training sets for the improvement and testing of density functional approaches and their parameters should be extended to include also more heavy atomic systems.

2. Calculational Details

Most of the calculations were carried out with the program packages TURBOMOLE 4.7 of Ahlrichs et al.^{51,52} and GAUSSIAN 98.⁹⁴ Ab initio MO–SCF (HF) and MP2⁵³ approaches were applied.

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(114) Perez-Jorda, J. M.; Becke, A. D. *Chem. Phys. Lett.* **1995**, 233, 134.

(115) Lauher, J. W.; Wald, K. *J. Am. Chem. Soc.* **1981**, 103, 7648.

In addition, SCF-DF calculations were carried out using several different versions of the *exchange-correlation DF*. We used (i) the simple local $X\alpha$ exchange potential suggested by Slater (S-LDF)⁵⁴ in 1951, with parameter $\alpha = 0.7$; (ii) the local correlation-corrected version developed by Vosko, Wilk and Nusair (SV-LDF) in 1980;⁵⁵ (iii) the additional nonlocal, i.e., gradient corrected (GGA) exchange potential of Becke (B) of 1988⁵⁶ and the additional nonlocal gradient-corrected correlation potential of Perdew (P) of 1986,⁵⁷ i.e., we used SVBP-GGA; (iv) the nonlocal exchange-correlation potential of Lee, Yang, and Parr (LYP-GGA);⁵⁸ and finally (v) Becke's three-parameter (B3) mixture of nonlocal Hartree-Fock ab initio exchange and LYP DF exchange-correlation, i.e., the B3-LYP-hybrid.⁵⁹

To reduce the number of electrons in the molecular complexes a bit, the inner core shells of gold were simulated by a *pseudopotential* operator. *Relativistic effects* are particularly important in the valence shell of gold; accordingly the relativistic spin-averaged, energy-adjusted, effective core potentials (RECP) from the Stuttgart group⁶⁰ were chosen. Spin-orbit effects are known to be small for Au(I) systems.⁶¹ To allow for a proper nodal structure of the gold valence shells and for proper outer core shell relaxation in the bonding processes (compare, e.g., refs 62,63), only the K, L, M, and N shells up to 4f were frozen (so-called small core), and the 19 'valence electrons' from the Au 5sp semicore and 5d6sp valence shells were treated explicitly. We did not apply the so-called Xe+4f medium core potentials.

The optimized contracted Gaussian *basis sets* of Schäfer, Ahlrichs et al. were applied. The valence triple- ζ plus one polarization type, TZVP,⁶⁴ which should yield qualitatively correct results at the DF level, below denoted by A, were used in most cases. The respective numbers of primitives and contractions for the different atoms are as follows: (5s1p)/[3s1p] for H; (11s6p1d)/[5s3p1d] for N and O; (14s9p1d)/[5s4p1d] for P, S, and Cl; (17s13p7d)/[6s5p3d] for Se; and (7s6p5d1f)/[6s3p3d1f] for Au (with $\alpha_f = 0.2$,⁴¹ good for outer polarization and longer distances). The latter basis is the one optimized for the RECP.

A few calculations with more *polarization functions* are denoted by A⁺. It had been pointed out by Pyykkö et al.⁴¹ that, at the ab initio correlated level, an additional, more compact f polarization function on gold ($\alpha_f = 1.2$) is very important for the Au d¹⁰ correlation. These not unexpected findings are corroborated by our own MP2, MP3, and MP4 calculations. For this type of theory, even a double f polarization basis may result in BSSE-counterpoise corrections as large as 50 kJ/mol. To come nearer to the basis set limit, even 3 f and 2 g functions were applied by Magnko et al.¹⁰⁵ The extension of the basis by compact f-AO sets on gold decreases the Au-Au equilibrium distances and increases the dimerization energies of (EAuL)₂ by 12 to 20 pm, and by 7 to 10 kJ/mol, respectively. The BSSE does not significantly change from the MP2 to the MP4 level, whereas the correlation energies have still not yet converged (see also, e.g., refs 41,47). On the other hand, it sounds reasonable that the compact f basis function has only a small influence on both the HF and DF MO-SCF results (a few pm, or kJ/mol, respectively, see below Figure 2(I)). Therefore, the application of the "smaller" A basis for these single configuration calculations seems justified.

For the *lighter* atoms, i.e., those other than Au and Se, also somewhat smaller basis sets were applied, namely the valence double- ζ plus polarization sets SVP:⁶⁵ (7s4p1d)/[3s2p1d] for N and O; and (10s7p1d)/[4s3p1d] for P, S, and Cl; and the SV (4s)/[2s] basis for the phosphinic H. This mixed basis was denoted by B. Finally, to speed up the integrations, compact auxiliary density basis sets were applied.^{52,67} The "counterpoise correction" (CC) of the BSSE⁶⁸ was applied to the Au-Au potential curves, thereby obtaining also BSSE-corrected structural, vibrational, and energetic parameters.

To analyze the Au-Au interaction in physical terms, Ziegler's approach⁶⁶ was used. The Au-Au attraction energy (E_{bond}) between the individually optimized fragments (which is slightly smaller than the one of the fully optimized cluster) is partitioned into three main contributions: (i) the Pauli exchange repulsion due to the overlap of

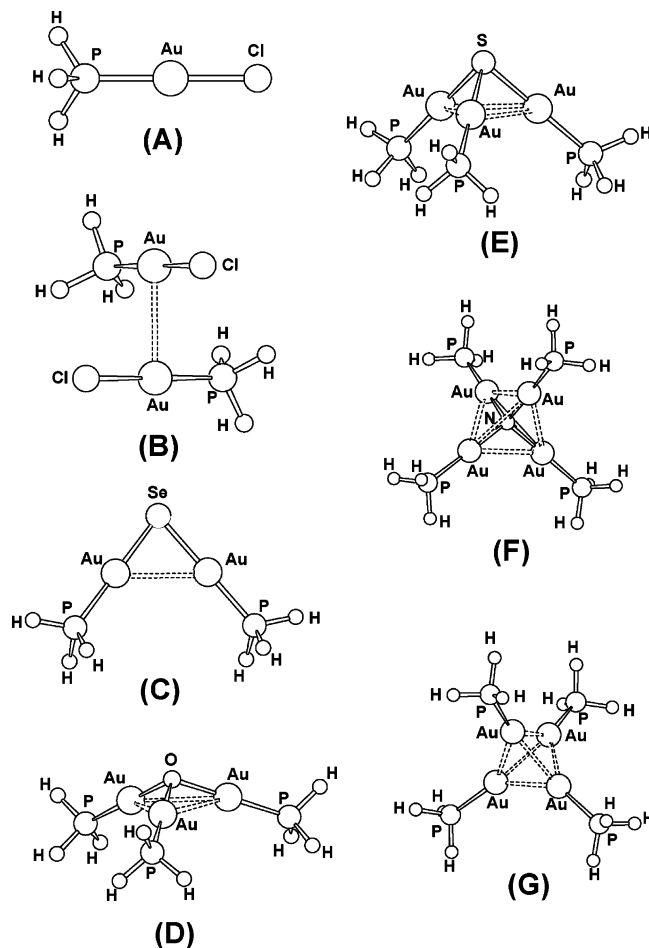


Figure 1. Structural formulas of different molecular gold compounds: (A) Cl-Au-PH₃; (B) Cl-Au-PH₃₂; (C) Se(Au-PH₃)₂; (D) O(Au-PH₃)₃⁺; (E) S(Au-PH₃)₃⁺; (F) N(Au-PH₃)₄⁺; and (G) (Au-PH₃)₄²⁺.

occupied orbitals of the independent fragments (E_{Pauli}); (ii) the electrostatic attractions and repulsions of the independent fragments' charge distributions (E_{elstat}); (iii) the orbital relaxation response (E_{orb}), comprising attractive quantum mechanical interference, charge transfer (donation and back-donation), polarization, and exchange-correlation effects. For this purpose, the Amsterdam Density Functional (ADF) code of Baerends et al.⁶⁷ was applied.

3. Results and Individual Discussions

3.1 E-Au-L Systems. 3.1.1 Cl-Au-PH₃ Monomer. Many gold cluster compounds are synthesized with the help of phosphines or related ligands, yielding e.g., (X-Au-PR₃)_n systems with R = Me, Et, *i*-Pr, *t*-But, Ph, etc.^{3,4,12} The computations were here performed with R = H. The optimized structural values of PH₃ obtained for the Cl-Au-PH₃ monomer (Figure 1A) were taken over for most of the other Au(I) cluster systems studied.

At first, we compare the fully optimized structures of the monomeric Cl-Au-PH₃ molecule in Table 1, as obtained by means of HF, MP2, and several DF computational methods, and by experiment (on solid phases, however). As known, ab initio HF is unable to reproduce reasonable bond lengths. From the cited literature, it is already known that Au bond lengths, as opposed to many other bonds, are overestimated at the HF level, in the present case by 5 pm for Au-Cl and by 10 pm for Au-P. With the correlation correction of MP2, both calculated bond lengths come to an agreement with the experimental values

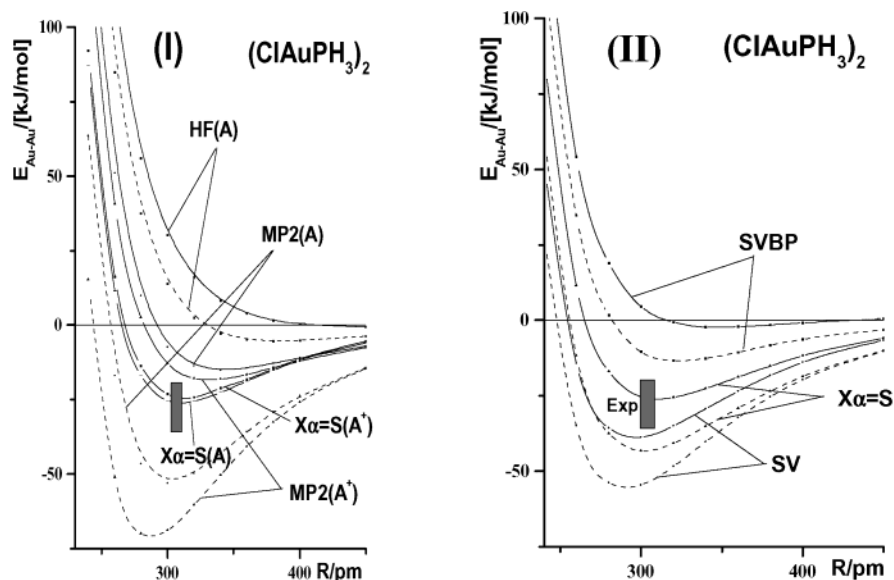


Figure 2. Auophilic interaction energy $E_{\text{Au-Au}}$ (in kJ/mol) between two relaxed ClAuPH_3 units, with BSS-error: - - -, and corrected by the CC: —, versus the Au-Au distance (in pm). (I): Comparison of HF, MP2 and $X\alpha = \text{S-LDF}$ with basis sets A and A^+ . (II): Comparison of three different DF approaches, $X\alpha = \text{S-LDF}$, SV-LDF, and SVBP-GGA (basis set A).

Table 1. ClAuPH_3 : Optimized Structures (interatomic distances R and bond angles θ)^a

method	basis	$R_{\text{Au-Cl}}/\text{pm}$	$R_{\text{Au-P}}/\text{pm}$	$R_{\text{P-H}}/\text{pm}$	$\theta_{\text{Au-P-H}}/\text{deg}$
HF	A	233.5	234.0	140.2	117.5
MP2	A	227.2	225.0	141.5	117.6
S-LDF	A	227.5	224.4	145.6	118.5
SV-LDF	A	225.4	221.6	143.4	118.4
SVBP	A	229.8	225.8	143.2	118.4
B3-LYP	A	230.7	228.1	142.1	118.2
HF [41]	1 of [41] ~ A	234.1	234.6	140.8	117.3
MP2 [41]	1 of [41] ~ A	227.9	226.6	141.4	117.3
MP2 [41]	3 of [41] ~ A^+	229.1	227.5	141.3	117.7
exp. ^b		~228	~224	~142	~118

^a Methods: HF = ab initio HF; MP2 = 2nd order Møller–Plesset; S-LDF = Slater- $X\alpha$; SV-LDF = Vosko–Wilk–Nusair; SVBP = Becke–Perdew 1986 GGA; LYP = Lee–Yang–Parr GGA; B3-LYP = Becke’s DF–HF Hybrid; exp = experimental. Basis sets: see section 2. ^b Average values for different phosphin ligands for molecules in condensed phase, see refs 4, 87, 110.

within 1 pm. This also holds for the simple S-LDF ($X\alpha$). The performance of the other DF approximations is mediocre. SVBP-GGA is still acceptable, whereas SV-LDF significantly underestimates and the B3-LYP hybrid significantly overestimates the bond lengths by several pm. Concerning the energetic parameters we note that previous calculations with S-LDF and SVBP yielded reasonable values for the chemical bonds to Au, compare also.^{16,43,44,69,103}

3.1.2 (Cl–Au–PH₃)₂ Dimer. Closed shell neutral atoms such as He, Be, Pd, or Xe form weak van der Waals bonded dimers. If the closed shell atoms carry positive charges such as Cs^+ , Cu^+ or Au^+ , then only excimers may exist, i.e., the ground states of M_2^{2+} possess repulsive potential curves only.^{36,70,71} However, when Au^+ is attached to Lewis bases such as in Cl–Au–PH_3 , the reduced electrostatic repulsions may be overcome by the “auophilic attraction”, particularly if the ligands are soft and electron-rich.^{39,41,72}

Pyykkö et al. had investigated the dimer $(\text{ClAuPH}_3)_2$ by means of ab initio SCF, MP2, MP3, MP4(SDQ), and CCSD-(T) techniques (the latter ones only at single points).^{36,41} More recent highest quality calculations were performed by Magnko

Table 2. $(\text{ClAuPH}_3)_2$ with Perpendicular Structure, See Figure 1B^a

method	basis	$R_{\text{Au-Au}}/\text{pm}$	$E_{\text{Au-Au}}/\text{kJ mol}^{-1}$	$k_{\text{Au-Au}}/\text{N m}^{-1}$
HF	B	∞ (~387)	0.1 (–5.2)	–(0.6)
MP2	B ^d	~338 (300)	–15 (–53)	8.6 (38)
	A^+	320	–25	15
S-LDF	B	308.7 (300.2)	–26 (–44)	22.0 (33)
SV-LDF	B	295.6 (290.4)	–39 (–56)	35.1 (46)
MP2 [36] ^c	2 ζ 1pol	350 (300)	–27 (–86)	
MP2 [41]	A/ A^+	~340/320	–15/–25	8/14
exp. ^b		~310	–20 to –40	

^a Calculated with BSSE-CC (BSSE uncorrected values in parentheses). Optimized Au–Au distances $R_{\text{Au-Au}}$, dimeric interaction energies $E_{\text{Au-Au}}$ and force constants $k_{\text{Au-Au}}$. For $R_{\text{P-H}}$ and $\theta_{\text{Au-P-H}}$ see Table 1. For the methods see caption of Table 1. ^b See refs 4, 5, 16, 26, 39, 41, 47, 72, 87, 89, 97, 110. ^c All Au–Cl, Au–P, P–H distances frozen. ^d Basis A and B not saturated for ab initio correlated calculations: too large $R_{\text{Au-Au}}$, too small $E_{\text{Au-Au}}$.

et al.¹⁰⁵ The Au–Au energy curves are quite flat so that the equilibrium distance becomes strongly dependent on small calculational errors such as the finite basis set, especially in the case of ab initio calculations. The importance of polarization functions on Au had already been mentioned in section 2. In addition, it must be admitted that even those quite sophisticated ab initio results may still differ significantly from the limiting values.^{41,105} We would now like to know, whether some specific DF works similarly well at much lower calculational cost for these intermediately overlapping Au–Au systems, and may it be just because of a fortuitous error cancellation. No systematic DF investigations in this respect are known to us.

Both present theory and previous experimental evidences^{72,107} show that the preferred structure of the free dimer with small ligands is the antiparallel eclipsed one, which results from the electrostatic attraction between the phosphine with positive partial charge (see below, section 4) and the negative chlorine, whereas the perpendicular form (Figure 1B) is quite common for larger ligands and in crystal phases. Results for the optimized perpendicular structure with internally frozen structure of the PH_3 ligands are shown in Table 2 and Figure 2. Concerning the present ab initio results, they resemble the previous ones of Pyykkö et al.^{36,41}

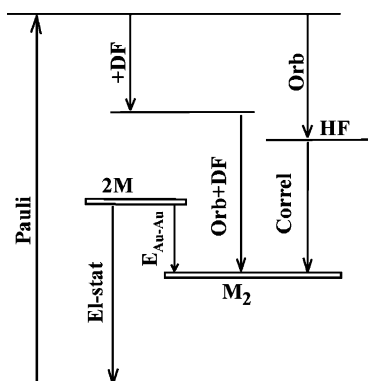


Figure 3. Qualitative break-down of auophilic attraction energies $E_{\text{Au-Au}}$ for the dimerization of two monomers, $2\text{M} \rightarrow \text{M}_2$. Left side and middle: Density functional approach. Left and right sides: ab initio approach. El-stat = electrostatic attraction between overlapping monomers; Pauli = ab initio Pauli repulsion; +DF = LDF contribution; Orb = ab initio orbital mixing (hybridization/polarization/interference); Orb+DF = orbital mixing effects at the DF level; HF = ab initio SCF; Correl = ab initio electron correlation (dispersion). Values correspond to ClAuPH_3 at $R_{\text{Au-Au}} = 3.1 \text{ \AA}$, assuming similar ab initio and DF energies of M_2 .

The structural and energetic S-LDF results agree reasonably well with the experimental estimates, which are $R_{\text{Au-Au}} \approx 310 \text{ pm}$ and $|E_{\text{Au-Au}}| \approx 20$ to 40 kJ/mol .^{4,5,16,26,39,41,47,72,87,89,97,110} SV-LDF shows overbinding ($R_{\text{Au-Au}}$ too short, $|E_{\text{Au-Au}}|$ rather large), as was also found in some related cases by Rösch et al.¹⁶ On the other hand HF, SVBP, and B3-LYP show underbinding. With MP2 we here obtain a somewhat small binding energy at a somewhat large distance, even with a double f polarization basis on Au (see also refs 36,41). As is well-known,^{2,39,41,100} the uncorrelated HF approach does not even yield a stable dimer.

The correction of the BSSE for such medium weakly bounded systems is important even for the present basis set, see Figure 2. The BSS-error shifts the potential curves down (by up to a few 0.1 eV), contracts the Au–Au equilibrium distances and increases the curvature (force constant k) significantly. As mentioned in section 2, the sensitivity to the BSSE is larger in the MP2 (0.2 to 0.3 eV, 0.3 to 0.4 Å, compare also⁶³) than in the DF approaches (0.05 to 0.1 eV, 0.02 to 0.05 Å).

Empirical relations exist between bond lengths, bond energies and force constants or vibrational frequencies. Concerning the Au–Au systems, the following linear regression for $R_{\text{Au(I)-Au(I)}}$ had been suggested^{73,74} for distances from 247 to 355 pm (see, however, ref 75)

$$R_{\text{Au-Au}} = 268 \text{ pm} + 29 \text{ pm} \cdot \ln([\text{N/cm}]/k_{\text{Au-Au}}) \quad (1)$$

The calculated force constants k at the S-LDF and SV-LDF levels are 0.22 and 0.35 N/cm, respectively, whereas our single and double Au-f-polarization-MP2 results of 0.09 and 0.15 N/cm are as low as Pyykkö's.² If we insert these k values into the empirical relation (1), then we obtain the following values for $R_{\text{Au-Au}}$: 312 pm (S-LDF), 298 pm (SV-LDF), 339 pm (1f-MP2), and 323 pm (2f-MP2), in good agreement with the theoretically optimized R values, see Table 2. That is, the calculated k – R data points lie near the correlation line (1) also in the region of weak bonds (as in Figure 8 of ref 74).

3.1.3 Analysis of the Auophilic Interaction Energy. A breakdown of the Au–Au binding energy at the S-LDF level is given in Table 3. At equilibrium Au–Au separation, the

Table 3. Breakdown of the $\text{Cl-Au-PH}_3 \cdots \text{Cl-Au-PH}_3$ Interaction Energy (perpendicular structure) at the S-LDF Level ($R_{\text{Au-Au}} = 3.1 \text{ \AA}$)

Pauli repulsion energy ^a of overlapping unperturbed monomers (a)	+164 kJ/mol
electrostatic attraction of overlapping unperturbed monomers (b)	–105 kJ/mol
sum of (a) and (b) (i.e., interaction of the unperturbed monomers)	+60 kJ/mol
orbital relaxation (c) ^b	–87 kJ/mol
total interaction energy ^c (sum of a,b,c)	–28 kJ/mol

^a Including exchange-correlation, i.e., the simulated dispersion attraction. ^b Hybridization, polarization, charge transfer, orbital interference. ^c With respect to the monomeric structures as in the dimer.

Table 4. Au–Au Density Overlap Σ (eq 3) and Au Orbital Populations $P(\text{Au-nl})$ of $(\text{ClAuPH}_3)_2$ (perpendicular structure, Figure 1B), Au_2 and the Monomers (S-LDF calculation)

	Au^+ (ref. value)	ClAuPH_3	$(\text{ClAuPH}_3)_2$ $R_{\text{Au-Au}} = 3.1 \text{ \AA}$	Au_2^{2+} $R_{\text{Au-Au}} = 3.1 \text{ \AA}$	Au_2^{2+*} $R_{\text{Au-Au}} = 2.47 \text{ \AA}$
$P(\text{Au}5d)$	–0–	–0.40	–0.43	–0.14	–0.26
$P(\text{Au}6sp)$	–0–	1.51	1.55	0.11	0.20
$\Sigma(\text{Au-Au})$	–0–	–0–	0.079	0.058	0.147

^a Au_2^{2+} at equilibrium distance of Au_2 .

overlap of the two unmodified monomers (see Table 4) is already large enough to result in quite strong Pauli repulsion. Without the S-LDF exchange-correlation correction, this repulsion would be even larger.

The penetration of the electron density cloud of one monomer into the cloud of the other monomer, where the nuclear attraction is only incompletely shielded, results in significant electrostatic attraction. This is so, although the Au(I) units are *formally* charged 1+. Because of electron donation by Cl^- and by PH_3 into the Au 6sp valence shell, the formal gold cation becomes nearly uncharged. According to Mulliken (or Ahlrichs) population analyses, presented in section 4, Cl^- donates 0.85 e (or 0.55 e, respectively) and PH_3 donates 0.3 e (or 0.35 e). The strong electrophilicity of Au is known to be related to the relativistic stabilization of its 6s and $6p^{1/2}$ orbitals, and the relativistic expansion/destabilization of the Au 5d shell contributes significantly to the electrostatic and dispersion attractions.^{63,90,100,101,106,107}

Although the repulsion between the two unperturbed monomers amounts to +60 kJ/mol, the self-consistently relaxed dimer (with electron correlation at the S-LDF level of approximation) becomes bound, namely by –26 kJ/mol through an energy lowering of –87 kJ/mol, due to orbital mixing. The latter is connected with comparatively small changes of the charge distributions and the atomic orbital populations (e.g., transfer of 0.04 e from the Au 5d to the 6sp shell). It comprises a covalent interaction of the partially occupied, overlapping Au 6sp valence shells, contributing about 22 kJ/mol.

3.2 E_{Au_n} and $E(\text{AuL})_n$ Systems. 3.2.1 SeAu_2^0 and $\text{Se}(\text{AuPH}_3)_2^0$. The V-shaped molecules $E^{V1}\text{M}_2$ and $E(\text{ML})_2$ are interesting because of the sensitivity of the M–E–M angle α (see Figure 1C) to the M–M interaction. In theoretical and experimental investigations on SCu_2 , SeCu_2 , etc., e.g.,^{47,76–79} angles below 90° and short M–M distances were found. We here investigate the molecules SeAu_2 and $\text{Se}(\text{AuPH}_3)_2$ (Tables 5 and 6), compare also.⁹¹ Correlation (i.e., the MP2 to HF difference) reduces the Au–Au distance and angle α of SeAu_2 and of $\text{Se}(\text{AuPH}_3)_2$ by about 60 pm and 18° , respectively. Local

Table 5. SeAu₂: Optimized Structures (for methods, see caption of Table 1)

method	basis	$R_{\text{Se-Au}}/\text{pm}$	$R_{\text{Au-Au}}/\text{pm}$	$\theta_{\text{Au-Se-Au}}/\text{deg}$
HF	A	244.0	359.1	94.7
	A ⁺	243.9	359.4	94.9
MP2	A ^b	238.7	298.7	77.1
	A ⁺	235.4	277.8	72.3
S-LDF	A	236.7	310.0	81.8
SV-LDF	A	234.2	298.2	79.1
	A ⁺	233.7	304.7	81.4
SVBP	A	238.5	340.5	91.1
LYP	A	261.5	356.4	84.1
B3-LYP	A	240.7	346.8	92.2
HF [36]	2 ζ 1pol	239.6 ^a	354.4	95.4
MP2 [36]	2 ζ 1pol	239.6 ^a	285.7	73.2

^a Fixed, nonoptimized value. ^b See footnote of Table 2.

Table 6. Se(AuPH₃)₂: Optimized Structures (for methods, see caption of Table 1)

method	basis	$R_{\text{Se-Au}}/\text{pm}$	$R_{\text{Au-Au}}/\text{pm}$	$R_{\text{Au-P}}/\text{pm}$	$\theta_{\text{Au-Se-Au}}/\text{deg}$
HF	B	245.5	368.1	239.8	97.1
MP2	B [§]	241.3	302.4	229.0	77.6
S-LDF	B	242.5	308.7	229.5	79.1
SV-LDF	B	239.6	299.9	226.2	77.5
SVBP	B	243.7	331.5	231.5	85.7
B3-LYP	B	244.5	348.1	234.1	90.8
HF [36]	2 ζ 1pol	239.6 ^b	361.1	225.4 ^b	97.8
MP2 [36]	2 ζ 1pol	239.6 ^b	293.0	225.4 ^b	75.4
exp. ^a		239–240	305	225–226	79.1

^a Se(AuPPh₃)₂ Ref. 15. ^b Fixed, nonoptimized value. [§] See footnote of Table 2.

density functionals (S, SV) give similar results as MP2 or experiment.¹⁵ When nonlocal exchange and correlation corrections are added (SVBP, LYP, B3-LYP), the Au–Au distance and Au–Se–Au angle increase, i.e., by about 40 pm and 10°, respectively. PH₃ ligands on Au modify α only weakly, what was already noted earlier.³⁶ Our HF and MP2 results are slightly different from ref 36, probably because we have optimized also the ligand-gold distances and angles and not kept them fixed. The inclusion of another f polarization function is not of that importance as at the DF level, as for (ClAuPH₃)₂. A second f polarization function is particularly important for ab initio correlation at larger Au–Au separations.

The halonium ions [X(AuL)₂]^{+120,121} are isoelectronic with the chalcogen derivatives E(AuL)₂. Although [Cl(AuPPh₃)₂]-ClO₄ has a similar structure with aurophilic bond and $\theta_{\text{Au-Cl-Au}} \approx 82^\circ$, the heavier halonium ions have open structures.

It is interesting to discuss the Au–Au overlap population (OP) values. For SeAu₂ at $R_{\text{Se-Au}} = 238\text{pm}$ and $\alpha = 80^\circ$ (i.e., near its equilibrium structure) they are 0.05 (ab initio HF), 0.06

Table 7. SAu₃¹⁺: Optimized Structures and C_{3v}–D_{3h} Energy Barriers ΔE_{Planar}

method	basis	$R_{\text{Au-S}}/\text{pm}$	$R_{\text{Au-Au}}/\text{pm}$	$\theta_{\text{Au-S-Au}}/\text{deg}$	$\Delta E_{\text{planar}}/\text{kJ mol}^{-1}$
HF	A		379.3(370.4)	105.0(105.9)	–19(–18)
MP2	A [§]	231.6	315.7(315.4)	86.0(85.7)	–98(–84)
S-LDF	A	226.3	329.3(318.8)	93.4(86.8)	–108(–111)
SV-LDF	A	223.9	320.2(297.7)	91.3(79.8)	–108(–117)
SVBP	A	229.0	343.1(345.0)	97.0(96.1)	–86(–87)
B3-LYP	A	232.4	350.9(350.9)	98.1(98.3)	–67(–67)
HF [40]	2 ζ	(232)	(361)	(102.3)	(–8)
MP2[40]	2 ζ	(232)	(302)	(80.5)	(–102)

Values in parentheses refer to Au–S fixed at a typical experimental distance of 232 pm. For methods see caption of Table 1. [§] See footnote of Table 2.

Table 8. S(Au–PH₃)₃¹⁺: Optimized Structures and C_{3v}–D_{3h} Energy Barriers ΔE_{Planar} ^a

method	basis	$R_{\text{Au-S}}/\text{pm}$	$R_{\text{Au-Au}}/\text{pm}$	$R_{\text{Au-P}}/\text{pm}$	$\theta_{\text{Au-S-Au}}/\text{deg}$	$\Delta E_{\text{planar}}/\text{kJ mol}^{-1}$
HF	B	239.7	384.9	238.3	106.8	–9
MP2	B ^f	235.2	313.4	229.1	83.6	–58
S-LDF	B	235.7	326.3	229.4	87.6	–41
SV-LDF	B	233.1	314.0	226.3	84.5	–45
SVBP	B	236.6	353.8	230.7	96.8	–31
B3-LYP	B	237.8	365.4	232.8	100.4	–25
HF ^b	2 ζ	(232)	(352)	?	(98.5)	(–15)
HF ^c	A ⁺	238.8	377.5	238.0	104.4	
MP2 ^b	2 ζ	(232)	(305)	?	(82.3)	(–113)
MP2 ^c	A ⁺	233.1	294.4	228.6	78.3	
exp. ^d		232	310	226	84	
exp. ^e		228.5(8)	325.3(1)	224.0(3)	90.8(4)	

^a Values in parentheses refer to Au–S fixed at a typical experimental distance of 232 pm. For methods see caption of Table 1. ^b Using a ‘large core’, 11-valence electron pseudopotential for Au, and fixed Au–S, Au–P distances [40]. ^c With ‘large core’ pseudopotential and optimized structure [47]. ^d Average values of distorted S(AuPPh₃)₃⁺ [80]. ^e Average structure of S[AuP(i-Pr)₃]₃⁺ [21]. ^f See footnote of Table 2.

(SVBP), 0.10 (S-LDF), and 0.04 (ab initio MP2). At the MP2 level, which describes a similarly strong Au–Au attraction as S-LDF, the OP is particularly low. This is because mixing in doubly substituted ionic configurations⁶³ populates non- and antibonding MO and enhances (for the appropriate mixing phase) the aurophilic attraction. On the other hand, the independent particle–MO–single configuration–DFT approach represents the aurophilic attraction by population of specially bonding MO. We note that orbitals, orbital energies, orbital populations, etc. have different meanings at different levels of theory. It is also a typical feature of quantum theory that different, physically equivalent theoretical representations or pictures of the same observable offer different complementary (noncontradictory, though sometimes counter-naive) explanations or interpretations.

3.2.2 SAu₃⁺ and S(AuPH₃)₃⁺. Crystalline [R₃PAu]₃S⁺ BF₄[–] contains isolated S(AuL)₃⁺ cations, where R may be Pr or Ph, for instance.^{21,80} The small Au–S–Au angles seem to indicate significant Au–Au attraction, although nonbonding interactions between PR₃ ligands also play a role. Still, for computational simplicity, we used L = PH₃. Results for SAu₃⁺ and S(AuPH₃)₃⁺ are shown in Tables 7 and 8.

Previous HF and MP2 results^{40,47,104} differ somewhat from the present ones, as well as from what might be expected from experiment,^{21,80} especially when a ‘large core’–small valence shell–pseudopotential was used for Au. Then the Au–Au distance comes out short. We have always used a ‘small core’ pseudopotential, and also optimized the S–Au distance. $R_{\text{S-Au}}$

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Table 9. OAu_3^+ : Optimized Structures and $C_{3v}-D_{3h}$ Energy Barriers $\Delta E_{\text{planar}}^a$

method	basis	$R_{\text{Au}-\text{O}}/\text{pm}$	$R_{\text{Au}-\text{Au}}/\text{pm}$	$\theta_{\text{Au}-\text{O}-\text{Au}}/\text{deg.}$	$\Delta E_{\text{planar}}/\text{kJ mol}^{-1}$
HF	A	207.7	359.7	120.0	0
MP2	A ^b	208.2	314.0	97.9	-19
S-LDF	A	205.4	298.4	93.1	-45
SV-LDF	A	204.1	289.6	90.6	-45
SVBP	A	206.3	322.7	102.9	-26
B3-LYP	A	206.8	340.7	110.9	-7.5
SV-LDF[16]	3 ζ 1pol	202	278		

^a See caption of Table 1. ^b See footnote of Table 2.

and α , $R_{\text{Au}-\text{Au}}$ are strongly correlated, as is demonstrated by the values in parentheses in Table 7.

The present fully optimized structural parameters of free $\text{S}(\text{AuPH}_3)_3^+$ agree reasonably well with the experimental crystal values of $\text{S}(\text{AuPPr}_3)_3^+$ and $\text{S}(\text{AuPPh}_3)_3^+$ at the MP2 and SV-LDF levels of theory, S-LDF yields interatomic distances at the upper acceptable limits, see Table 8. The nonlocal, improved DFT versions (SVBP, B3-LYP) again underestimate the Au–Au attraction. We note the strong dependence of the structure upon attaching ligands, compare Tables 7 and 8. This seems to be in line with the experimentally found sensitivity of the structural data on aliphatic or aromatic phosphine ligands, whereas the above-mentioned reference did not support this view.⁴⁷

3.2.3 OAu_3^+ and $\text{O}(\text{AuPH}_3)_3^+$. The lighter homologues of the sulfonium compounds are the oxonium ones.^{47,81,82} The $\text{O}(\text{AuPR}_3)_3^+$ cation moieties tend to dimerize in the crystal with interionic Au–Au separations slightly larger than 3 Å. Our model calculations on single, free OAu_3^+ and $\text{O}(\text{AuPH}_3)_3^+$ are presented in tables 9 and 10.

Isolobal OH_3^+ has H–O–H angles of 112° at the MP2 level, which coincides with the best estimates, e.g.,⁸³ whereas the bigger triauroxonium species have smaller angles, around 95° for OAu_3^+ ; around 105° for $\text{O}(\text{AuPH}_3)_3^+$; and 104° for $\text{O}(\text{AuP}(i\text{-Pr})_3)_3^+$. Without the correlation corrections at the MP2 or local DF (S or SV) levels, the pyramidal angle is obtained too large, by the order of 10° to 15° for the SVBP and B3-LYP approaches, whereas at the ab initio SCF level the trigonal pyramids become even planar (angle 120°). Previous results^{16,47} differ from the present ones and from the experimental data. The latter refer to bigger ligands and to the condensed, neutral phase with counterions. Interionic aurophilic attraction energies of the order of 25 to 35 kJ/mol were determined by NMR techniques for the dimers.

3.2.4 NAu_4^+ and $\text{N}(\text{AuPH}_3)_4^+$. Tetravalent atoms or ions form tetragold species with centered tetrahedral or distorted structures,^{57,84,85} see Figure 1 F,G. The present results of naked NAu_4^+ and $\text{N}(\text{AuPH}_3)_4^+$ are shown in Tables 11 and 12. For NAu_4^+ we find rather similar energies for the two different structures, centered tetrahedral (T_d) and capped tetragonal (C_{4v}), with differences of +10 and -10 kJ/mol at the MP2 and S-LDF levels, respectively, whereas a ‘large core’ MP2 calculation³⁷ reported a stronger tendency toward C_{4v} at rather large bond lengths. Our results, however, agree with more recent calculations using a ‘small core’.⁴⁷ Our ab initio HF and nonlocal DFT (SVBP, B3-LYP) also yield too long N–Au distances, while MP2 as well as S-LDF and SV-LDF perform comparably well.

3.3 Empty Au_4 Tetrahedra. 3.3.1 Au_4^{q+} and $(\text{AuPH}_3)_4^{q+}$. Following the idea of strong 2-electron polycentric (2e-nc)

Table 10. $\text{O}(\text{Au}-\text{PH}_3)_3^+$: Optimized Structures and $C_{3v}-D_{3h}$ Energy Barriers $\Delta E_{\text{planar}}^a$

method	basis	$R_{\text{Au}-\text{O}}/\text{pm}$	$R_{\text{Au}-\text{Au}}/\text{pm}$	$R_{\text{Au}-\text{P}}/\text{pm}$	$\theta_{\text{Au}-\text{O}-\text{Au}}/\text{deg.}$	$\Delta E_{\text{planar}}/\text{kJ mol}^{-1}$
HF	B	205.2	355.5	232.4	120.0	0
MP2	B	204.3	324.1	224.8	105.0	-5
S-LDF	B	204.2	330.2	224.3	107.9	-5
SV-LDF	B	202.3	320.9	221.4	105.0	-5
SVBP	B	205.8	342.9	225.2	112.8	-2
B3-LYP	B	205.1	355.3	226.8	120.0	0
HF [47]	A ⁺	204.8	354.8	233.3	120.0	
MP2 [47]	A ⁺	202.9	298.1	224.8	94.6	
SV-LDF [16]	3 ζ 1pol	202	288	217	91	
exp. ^a		203.0(3)	319.8(1)	222.8(2)	103.7(2)	

^a See Also Caption of Table 1. ^b $\text{O}[\text{AuP}(i\text{-Pr})_3]_3^+$ ref 81.

Table 11. NAu_4^+ : Optimized Structures (yielding T_d symmetry)^a

method	basis	$R_{\text{N}-\text{Au}}/\text{pm}$	$R_{\text{Au}-\text{Au}}/\text{pm}$
HF	B	207.6	339.0
MP2	B	201.3	328.7
S-LDF	B	198.0	323.3
SV-LDF	B	195.8	319.7
SVBP	B	201.5	329.1
B3-LYP	B	203.9	333.0
HF ^b	2 ζ	216.2	353.0
MP2 ^b	2 ζ	216.0	352.7

^a See also caption of Table 1. ^b Using a ‘large core’ for Au ref 37.

Table 12. $\text{N}(\text{AuPH}_3)_4^+$: Optimized Structures (yielding T_d symmetry)^a

method	basis	$R_{\text{N}-\text{Au}}/\text{pm}$	$R_{\text{Au}-\text{Au}}/\text{pm}$	$R_{\text{Au}-\text{P}}/\text{pm}$
HF	B	206.8	337.7	236.0
MP2	B	202.0	329.8	227.6
S-LDF	B	203.0	331.5	227.8
SV-LDF	B	200.5	327.4	224.6
SVBP	B	205.4	335.3	228.9
B3-LYP	B	206.2	336.7	231.0
HF ^b	2 ζ	214.7	305.5	
HF ^c	A ⁺	206.0	336.5	235.2
MP2 ^b	2 ζ	213.2	348.1	
MP2 ^c	A ⁺	198.1	323.4	227.1
exp. ^d		201.6	328.6	

^a See caption of Table 1. ^b ‘Large core’ for Au, fixed Au–P distance, ref. 37. ^c ‘Small core’ for Au, optimized Au–P distance, ref. 47. ^d Average of distorted $\text{N}(\text{AuPPh}_3)_4^+ \text{F}^-$ ref. 84.

bonding, e.g.,¹⁰ $[\text{AuP}(t\text{-But})_3]_2^{2+}$ salts could be synthesized,⁸⁶ thereby demonstrating the stability of ligated empty Au_4^{2+} groups with a doubly occupied, strongly binding 4-center orbital of a_1 species, winning against the internal Coulomb repulsion energy. As before, S-LDF yields similar structures as MP2, see Table 13. Because of the central polycenter covalence in addition to the peripheral aurophilic attractions, the Au–Au distances are now shorter, around 270 to 275 pm. Still, SVBP and in particular B3-LYP overestimate the Au–Au distances, here by about 10 pm, whereas pure aurophilic ‘bond lengths’ were typically overestimated by 20 pm.

Concerning Au_4^{4+} , it is, as expected, completely unstable against Coulomb explosion, whereas it is an interesting question whether $(\text{AuPR}_3)_4^{4+}$ becomes meta-stabilized due to the combined effect of aurophilic attraction and improved charge delocalization. That is, the four $\text{P}\rightarrow\text{Au}^+$ donor bonds may be stabilized by mixing with the otherwise empty, lowest $(\text{Au}6\text{sp})_4$ orbitals of a_1 and t_2 type, thereby stabilizing the Au cluster. Our calculations for R = H (Table 14) support this expectation, yielding a typical aurophilic $R_{\text{Au}-\text{Au}}$ of about 3 Å. This

Table 13. Au₄²⁺ and (Au–PH₃)₄²⁺: Interatomic Distances of Optimized Structures of T_d Symmetry^a

method	basis	R _{Au–Au} /pm for Au ₄ ²⁺	R _{Au–Au} /pm for (AuPH ₃) ₄ ²⁺	R _{Au–P} /pm for (AuPH ₃) ₄ ²⁺
HF	B	293.5	292.5	245.7
MP2	B	277.7	275.8	232.7
S-LDF	B	273.2	276.2	232.8
SV-LDF	B	269.1	274.2	229.7
SVBP	B	277.0	280.2	235.0
B3-LYP	B	281.5	285.2	238.0
HF [38]	A	292.0	289.9	
MP2 [38]	A	272.3	271.8	
exp. ^b			270–273	230–231

^a See also caption of Table 1. ^b [AuP(*t*-Bu)₃]₄²⁺ ref 86.

Table 14. (AuPH₃)₄⁴⁺: Interatomic Distances of Optimized Structures of T_d Symmetry

method	basis	R _{Au–Au} /pm	R _{Au–P} /pm
HF	B	454.2	242.0
MP2	B	304.2	233.4
S-LDF	B	295.5	234.9
SV-LDF	B	287.8	231.9
SVBP	B	∞	227.1
exp. ^b		(≥307)	(~227)

^a See also caption of Table 1. ^b Strongly flattened Au tetrahedron in [X₂(AuPH₃)₄]²⁺ ref. 121.

Table 15. (AuGeH₃)₄^{q-}: Interatomic Distances of Optimized Structures (T_d Symmetry)^a

q	method	basis	R _{Au–Au} /pm	R _{Au–Ge} /pm
0	S-LDF	B	281.8	243.5
	S-LDF	A ⁺	284.5	243.3
	SV-LDF	B	277.0	240.0
	SV-LDF	A ⁺	279.6	239.8
2–	S-LDF	B	280.2	246.1
	S-LDF	A ⁺	282.1	246.0
	SV-LDF	B	275.8	242.5
	SV-LDF	A ⁺	277.8	242.3

^a See also caption of Table 1.

demonstrates the important role of the ligands in Au(I)-cluster systems. Without any correlation correction, the HF approach gives significantly too long Au–Au distances, and that happens also for the nonlocal DF potentials.

Without A[–] counteranions, the Au₄⁴⁺ moiety, either with or without ligands, is unstable in the absolute sense. However, (AuPR₃)₄⁴⁺ (A[–])₄ should exist in the condensed phase for appropriate ligands and anions. We have learned only recently that similar clusters have already been synthesized.¹²¹ [X₂(AuPR₃)₄]²⁺ (A[–])₂, with halogen X and large anion A contains a gold tetrahedron distorted toward a puckered square, where the two long ‘diagonal’ Au–Au distances are nearly right-angled capped by X[–] units, see Table 14.

3.3.2 (AuGeH₃)₄ and (AuGeH₃)₄^{2–}. (AuGeH₃)₄ and (AuGeH₃)₄^{2–} (see Table 15) are iso-valence-electronic with (AuPH₃)₄⁴⁺ and (AuPH₃)₄²⁺, respectively, having 4 and 5 valence electron pairs on the tetrahedral Au₄E₄ unit. Although the additional electron pair on (AuGeH₃)₄^{2–} should increase the total bond order in comparison to (AuGeH₃)₄, the repulsion of the two negative charges counterbalances this so that there is no significant change of the equilibrium structure of the central Au₄ unit (R_{Au–Au} in both cases is about 2.8 Å). In contrast, the larger Coulomb repulsion energy and the smaller number of valence electron pairs on (AuPH₃)₄⁴⁺ results in a much larger

Table 16. Mulliken Populations and Charges of E(AuL)_n^{q+} at the S-LDF Level (basis B)

system	symm.	Au6s	Au6p	Au5d ^z	Au5f	Au	E	PH ₃
ClAuPH ₃	C _{3v}	1.16	0.36	–0.40	0.06	–0.17	–0.14	0.31
(ClAuPH ₃) ₂	C ₂	1.14	0.41	–0.43	0.07	–0.19	–0.13	0.30
SeAu ₂	C _{2v}	1.06	0.11	–0.29	0.03	0.03	–0.05	
Se(AuPH ₃) ₂	C _{2v}	1.16	0.37	–0.41	0.05	–0.17	–0.24	0.30
NAu ₄ ⁺	T _d	0.86	0.08	–0.47	0.01	0.52	–1.10	
N(AuPH ₃) ₄ ⁺	T _d	1.16	0.30	–0.51	0.04	0.01	–0.71	0.42
OAu ₃ ⁺	C _{3v}	0.70	0.12	–0.32	0.04	0.46	–0.39	
	D _{3h}	0.64	0.08	–0.30	0.02	0.55	–0.65	
O(AuPH ₃) ₃ ⁺	C _{3v}	1.10	0.27	–0.48	0.05	0.06	–0.47	0.43
	D _{3h}	1.09	0.27	–0.48	0.05	0.06	–0.52	0.44
SAu ₃ ⁺	C _{3v}	0.86	0.12	–0.31	0.03	0.30	0.11	
	D _{3h}	0.75	0.10	–0.26	0.03	0.39	–0.16	
S(AuPH ₃) ₃ ⁺	C _{3v}	1.12	0.28	–0.32	0.05	–0.06	–0.01	0.40
	D _{3h}	1.11	0.27	–0.32	0.04	–0.04	–0.15	0.43
Au ₄ ²⁺	T _d	0.61	0.10	–0.25	0.03	0.50		
(AuPH ₃) ₄ ²⁺	T _d	1.15	0.22	–0.39	0.05	–0.04		0.54
(AuPH ₃) ₄ ⁴⁺	T _d	1.11	0.11	–0.32	0.04	0.06		0.94

^a With respect to d¹⁰.

Au–Au distance (R_{Au–Au} = 3.0 Å) than in the case of (AuPH₃)₄²⁺ (R_{Au–Au} = 2.7 Å). We have not yet found examples in the experimental literature, whereas Au–Au di-gold (R_{Au–Au} = 294 pm) and Au–Au–Au–Au tetra-gold chain molecules with Au–Ge and/or Au–As bonds are known.¹²²

4. General Comments on the Aurophilic Interaction

4.1 Effective Charges on Au. The effective Mulliken charges (Table 16) on the gold atoms of EAu_n^{q+} vary with formal charge +q/n and with electronegativity of E between 0 and 0.5+, corresponding to 0.2 to 0.5 electron holes in the 5d shell, to 0.6 to 1.1 e in the 6s and ~0.1 e in the 6p valence shells. The soft base PH₃ ligands transfer 0.3 or more electronic charges onto the Au^{δ+} atom, so that *the gold atoms carry only very small positive or even slightly negative effective charges.* (Ahlrichs’ MAO-charges,⁹³ which are nearly basis set independent, have also been determined in a few cases; they are similarly small.) In these cases the nearly vanishing charge on gold goes, on the broad average, with 0.4 ± 0.1 electron holes in the Au5d shell, and with ~1.1 e in the 6s and ~0.3 e in the 6p valence shells. The increased p population reflects the linear coordination of the Au atom. The small effective charges on Au seem to enhance the Au(I)–Au(I) attraction, compare for instance the equilibrium distances and charges of the different [O,S](Au[÷,PH₃])₃⁺ and (Au[÷,PH₃,GeH₃])₄^{q+} species with each other. We note that the effective charges in Table 16 are the *gross* values (also discussed in ref 33). They are the sum of the atomic net charges (which are significantly more positive; they were used for discussions by Pyykkö et al.⁹⁴) and of one-half each of the respective bond charges. The gross atomic charges seem more useful in the present context for qualitative explanations than the net charges or the even bigger formal charges. That is, one should not argue that a strong Coulomb repulsion between formally charged Au atoms must at first be overcome when forming polymers of (X–Au⁺L)_n. There is no such electrostatic repulsion for the cases of small effective gross charges.

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4.2 Electrostatic Overlap Interactions. If closed shells overlap, then classically the electronic shells of one atom are attracted by the incompletely shielded other nucleus, and vice versa. Pyykkö³⁷ noted the low or even slightly negative binding overlap for Au–Au around 3 Å. A common measure of *wave function* overlap population P between two atoms A,B is Mulliken's expression

$$P_{AB} = 2 \sum_{i \in A} \sum_{j \in B} (D_{ij} \cdot S_{ij}) \quad (2)$$

where D and S are the density and overlap matrixes in the basis of atomic orbitals. Because bonding and antibonding overlap contributions are of opposite sign, they counteract each other in P . Small P can therefore also correspond to significant *density* overlap. An expression to represent the latter, where both types of overlap sum up, independent of the phase of the wave functions, is

$$\Sigma_{AB} = 2 \left[\sum_{i \in A} \sum_{j \in B} (D_{ij} \cdot S_{ij})^2 \right]^{1/2} \quad (3)$$

As shown in Table 4, the density overlap of two Au⁺ increases with decreasing distance, approximately as $6 \cdot e^{-R/\text{Å}}$. The density overlap of (Cl[−] → Au⁺ ← L)₂ is larger, at the same Au–Au separation, than of (Au⁺)₂ corresponding to the increased Au6s occupation in (ClAuL)₂. The density overlap leads to a significant electrostatic attraction (Table 3) of the *formally* positively charged Au(I) species.

4.3 Partial Overlap Repulsion. In addition to classical electric attractions, quantum mechanically there is the Pauli exclusion repulsion between the occupied shells (see Figure 3). If an occupied shell is near-degenerate with an empty shell, such as ns² and np⁰ of the Be⁰ isoelectronic atoms, or nd¹⁰ and (n+1)sp⁰ of Au¹⁺ type ions, then polarization, deforming the closed shell, is rather easy so that the Pauli repulsion increases less strongly than usually at distances below the van der Waals separation. A comparatively low SCF repulsion was also mentioned by Magnko et al.¹⁰⁵ On the other hand, for heavy atomic systems with high nuclear charge and many electrons in the outer shells, the electrostatic attractions become significant. Thus, the two opposing factors cancel each other to a significant extent so that some small additional attractions are sufficient to create a weak binding. Environmental influences by counterions and solvent molecules were mentioned in this respect by Schmidbaur et al.¹²¹ For a more comprehensive discussion of 'secondary' bonds see ref 98.

4.4 Orbital Interactions. In addition to the Pauli repulsion (i.e., increase of kinetic energy due to orthogonalization of overlapping occupied orbitals), the occupied *one-electron orbitals* can be mixed with virtual ones as a response to the electrostatic and Pauli interactions. As Tables 4 and 16 show, the two nucleophilic ligands create a hole in the Au 5d shell of up to half an electron and simultaneously transfer electronic charge into the Au 6s and 6p shells. An additional auophilic interaction upon dimerization increases the 5d hole and the 6s–6p occupation only slightly. Still there is a significant energy lowering accompanying the orbital hybridizations and relaxations (Table 3).

At the DFT level, the *two-electron correlation* effects, as represented by the HF-MP2 energy difference (see Figure 2),

Table 17. Deviations ('estimated errors') Δ of Calculated Auophilic Distances $R_{\text{Au–Au}}$ (in pm) and Interaction Energies $E_{\text{Au–Au}}$ (in kJ/mol) from Experimental Estimates of Different Compounds, and Average Deviations Δ (with $1 \cdot \sigma$ in Parentheses), See also Caption of Table 1

method	ab initio		DFT			
	HF	MP2	S-LDF	SV-LDF	SVBP	B3-LYP
(ClAuPH ₃) ₂	∞	~ +25	−1	~ −14	~ 41	
Se(AuPH ₃) ₂	63	−2.5	4	−5	~ 26	~ 40
S(AuPH ₃) ₃ ⁺	60	~ −10	1	~ −11	~ 29	~ 40
O(AuPH ₃) ₃ ⁺	36	4	10	1	~ 23	~ 35
N(AuPH ₃) ₄ ⁺	9	1	3	−1	~ 7	~ 8
(AuPH ₃) ₄ ²⁺	21	4	5	3	~ 9	~ 15
(AuPH ₃) ₄ ⁴⁺	~50	~2	~−5	~−15	∞	
Au ₄ ²⁺	~20	~3	~−2	~−6	~2	~7
(AuGeH ₃) ₄			~0	~−5		
(AuGeH ₃) ₄ ^{2−}			~0	~−4		
Hg ₂	~35	~13	~0	~−18	~60	~60
$\Delta R_{\text{Au–Au}}/\text{pm}$	+50(30)	+3(10)	+4(5)	−5(10)	+25(15)	+30(20)
$\Delta R_{\text{Au–E}}/\text{pm}$	+10(10)	+1(2)	+0(3)	−2(2)	+2(4)	+4(3)
$\Delta E_{\text{Au–Au}}/\text{kJ mol}^{-1}$	+40(40)	+3(2)	−3(20)	−6(15)	+13(15)	+25(20)

are approximately included in the Pauli and orbital relaxation terms (see Figure 3). In the even simpler semiempirical approaches, the SCF operator matrix elements are directly adjusted to reproduce correlated bond energies. In both cases, the correlation effects at overlap-distances are immersed in the effective one-particle terms. Long range correlations are not yet completely accounted for in the present day DF and semiempirical procedures; this is just one argument more to improve them on a theoretical basis.

In summary, when the Au(I) closed shells approach each other, the Pauli overlap repulsion increases comparatively slowly, whereas the electrostatic overlap attraction (!) increases significantly enough so that the combined effect of orbital mixing and electron correlation adds up to a 'secondary bond'. Electron donating ligands trigger the auophilic attraction by varying the effective atomic charges, the populations of the hybridizing 6sp valence orbitals, and the flexibility of the 5d shell with its partial hole. Magnko et al.¹⁰⁵ had pointed out that the metal's d¹⁰ closed shell, the metal's virtual orbitals and the ligands' occupied and virtual orbitals all participate in quantum mechanical Pauli repulsion and orbital attraction, in electrostatic and polarization attractions, in van der Waals long range and in charge transfer shorter range correlation attractions, and in repulsive correlation contributions. Because dispersion is only one contribution, it is not clear from the beginning, whether DFT will fail to reproduce these secondary interactions.

4.5 DFT and the Auophilic Interaction. The overall performance of the different approaches, concerning the Au–Au distances (in some detail) and also the energies, is displayed in Table 17. Concerning the auophilic distances, ab initio correlation corrected methods such as MP2 work as well as Slater's LDF ($\Delta R_{\text{Au–Au}} \approx 5$ pm, $\Delta E_{\text{Au–Au}} \approx 5$ kJ/mol), and SV-LDF is still acceptable for qualitative investigations. With a little reservation this holds for the auophilic interaction energies too. The literature statement that DFT cannot reproduce the auophilic attractions at all, cannot be substantiated here in this generality.

However, it must be admitted that concerning different types of molecules, the standard errors of the DFT Au–Au binding energies are 1 order of magnitude larger than the ab initio MP2 ones; they reach to the order of the $E_{\text{Au–Au}}$ values itself. This is compatible with the conjecture that S-LDF (and still also SV-

LDF) works because of fortuitous cancellation of errors. On the other hand modern GGA approaches and their parameters have been selected upon their performance for light and medium light elements. So, S-LDF may be used for cursory surveys of heavy element compounds, whereas it is advisable to investigate individual crucial cases by more demanding, but more reliable ab initio post SCF methods (the same as for LDF may hold for semiempirical MO approximations). However, ab initio HF-MO as well as common gradient improved DF approaches such as SVBP, LYP, or B3-LYP are not useful at all. Indeed, simple LDF approaches were successfully used by researchers such as Hargittai, Laguna, Molina, Rösch et al.^{16,24,43–45,91,99,102,104,109} and also by ourselves.^{69,119} Instead of all-electron approaches, also pseudopotential (or frozen core) approaches work well, but

only if the so-called small-core versions are applied, where the 5spd shells of Au are treated as relaxing 'valence shells'.

On the basis of the present LDA calculations we suggest the experimental search for 'tetrahedral' compounds $[(\text{AuPR}_3)_4]^{4+}$ (A^-)₄, $[(\text{AuGeR}_3)_4]$, or $[(\text{AuGeR}_3)_4]^{2-}$ (B^+)₂ with anions A^- and cations B^+ .

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