Relativity, Gold, Closed-Shell Interactions, and $CsAu \cdot NH_3$

Pekka Pyykkö*

The chemical properties of gold are strongly influenced by relativistic effects. One example is the large electronegativity of Au, which qualitatively explains the stability of (solid or liquid) cesium auride, Cs^+Au^-, and other systems with Au^- ions. An especially impressive compound is $CsAu \cdot NH_3$, the structure and bonding of which are discussed. Future possibilities for finding further aurides are outlined.

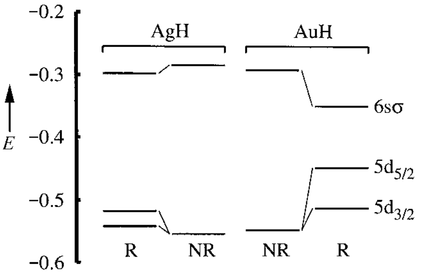

Figure 1. The relativistic (R) and nonrelativistic (NR) orbital energies of AgH and AuH. The data are taken from Desclaux and Pyykkö,[1] who concluded from them and the bond length data "*…that the chemical difference between silver and gold may mainly be a relativistic effect.*" E in Hartree.

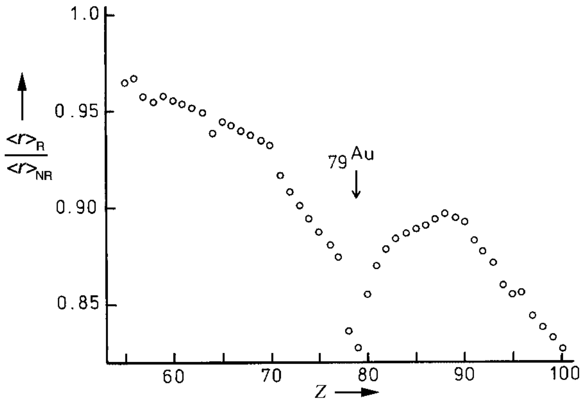

Figure 2. The ratio of relativistic ($\langle r \rangle_R$) and nonrelativistic ($\langle r \rangle_{NR}$) 6s-shell radii in the atomic ground states of the elements 55–100 (reproduced from Pyykkö and Desclaux;[3] copyright © 1979 American Chemical Society).

Relativity and Gold

Relativistic effects in chemistry are due to the high speeds of electrons when they move near a heavy nucleus. These effects can be described by the Dirac equation, or some approximation to it, and explain many of the differences and some of the similarities between the fifth and sixth row of the periodic table. A well-known example is the case of silver versus gold. These valence-shell relativistic effects increase roughly like Z^2, where Z is the full nuclear charge, and become comparable in size with various shell structure effects on the 6th row ($Z = 55-86$).

To be more specific, the nonrelativistic ("NR") 5d and 6s orbital energies of Au are similar to the 4d and 5s orbital energies of Ag, whereas the relativistic energies ("R") are not, both in the metal atoms M and in their diatomic hydrides MH.[1–3] The original data of ref. [1] are shown in Figure 1. The relativistic bond length contraction also behaves roughly as Z^2 and is able to pull in Au–L (L = ligand) single bond lengths to, or below, those of the corresponding Ag–L, and to make the Au–L bond strengths at the same time larger than those of the corresponding Ag–L.[1, 4]

A further particularity is that, along a row, from Group 1 to Group 18, there is a local gold maximum[3–5] of relativistic effects at Group 11 (for all coinage metals, Cu–Au), thereby making these elements more "relativistic" than their left-hand or right-hand neighbors. Such a local maximum is seen in all properties of the ns shells (for an example, see Figure 2). This anomaly can be qualitatively ascribed to the interaction of relativistic effects and shell structure effects, caused in particular by the overlap between the $(n-1)$d and ns shells. Figure 2 has not only gone into textbooks[6] but has become a bit of an icon for the world's gold industries.[7] In quantum chemistry the simple molecules AuH and Au_2 have become classical test cases for relativistic effects.[1, 8, 9] The most accurate benchmark results[10–13] on these two molecules are reproduced in Table 1.

A wide literature exists on relativistic calculations on gold compounds. There are predictions for subsequently observed new species, such as diatomic AuF (predictions in ref. [15, 16], observation in ref. [16]) or the first triple bond to gold in $Au{\equiv}C^+$ (prediction in ref. [17], observation in ref. [18]). The possibility of covalent chemical bonds between gold and

---

[*] Prof. P. Pyykkö
Department of Chemistry, University of Helsinki
P.O.B. 55 (A.I. Virtasen aukio 1), 00014 Helsinki (Finland)
Fax: (+358) 9-191-50169
E-mail: Pekka.Pyykko@helsinki.fi

Table 1. Latest relativistic benchmark results on AuH and Au_2 and the corresponding nonrelativistic reference values. Bond lengths R_e in pm, vibrational frequencies ω_e in cm^{-1}, and dissociation energies D_e in eV. Note the agreement between all-electron (AE) and pseudopotential (PP) methods.

Molecule	R_e	ω_e	D_e	Method	Ref.
AuH	175.0	1565	1.79	NR AE CCSD(T)	[10]
	152.5	2288	2.92	R AE CCSD(T)	[10]
	174.7	1575	2.086	NR PP CCSD(T)	[11]
	152.7	2306	3.124	R PP CCSD(T)	[11]
	151.0	2330	3.31	R PP CCSD(T)	[12]
	152.4	2305	3.36	exp.	[12]
Au_2	248.8	187	2.19	R AE cp-CCSD(T)	[13]
	249.0	187	2.23	R PP CCSD(T)	[12]
	247.2	191	2.302(8)	exp.	[14]

xenon in species like $AuXe^+$ and $XeAuXe^+$ was pointed out in ref. [19]. Meanwhile, both species have been observed by mass spectrometry.[20] Several bulk compounds with covalent Au–Xe bonds, such as $(AuXe_4)(Sb_2F_{11})_2$, have recently been synthesized and theoretically studied;[21–23] for comments on [21], see ref. [24].

The higher gold hydrides AuH_3 [$(H_2)AuH$] and AuH_5 [$(H_2)AuH_3$] were observed in matrices.[25] Numerous studies exist on gold clusters (see for example ref. [26, 27]). The role of relativity in the change of the oxidation state from Au^I to Au^{III} in halide complexes has been explicitly demonstrated.[28] A wide field are the studies of the aurophilic attraction between Au^I ions in compounds.[29, 30] This attraction turned out to be a dispersion (van der Waals) effect, strengthened by relativistic effects for gold. Its strength can reach that of a strong hydrogen bond. Typical Au^I–Au^I equilibrium distances, R_e, are about 300 pm. For the latest theoretical study, analyzing the various detailed contributions, see ref. [31].

Against this background, exactly how large are the relativistic effects on various observable properties of the gold atom or of metallic gold? The latest available answers are given in Tables 2 and 3, respectively. For the first ionization potential, IP1, of gold it is seen that the best relativistic calculation deviates from the experimental value, which is very accurate, by only 0.0285 eV, while the corresponding nonrelativistic value lies 2.169 eV below the experimental one. (The NR limits can often be taken by using the same approximations but a very large speed of light.) For the electron affinity, EA, of gold—of special importance here—the best relativistic calculation is 0.014 eV and the nonrelativistic one 1.026 eV below the experimental value. Notably, almost half of the electron affinity of gold comes from relativity; the calculated NR value for gold is close to that of silver. The experimental EA of gold (2.30861(3) eV) is not qualitatively different from that of iodine, 3.059038(10) eV.[32]

Table 2. Atomic properties of some noble metals.

Property	Cu	Ag	Au	111	Pt
electronic configuration	$3d^{10}4s^1$	$4d^{10}5s^1$	$5d^{10}6s^1$	$6d^97s^2$	$5d^96s^1$
EA [eV]					
experimental[a]	1.23578(4)	1.30447(2)	2.30861(3)	1.56[33]	2.12510(5)
calculated[b]		1.350	2.295		
calculated[c]		1.140	1.283		
IP1 [eV]					
experimental[d]	7.72636(2)	7.576237(25)	9.22554(2)	10.6[e]	
calculated[b]		7.512	9.197		
calculated[c]		6.948	7.057		
IP2 [eV]	20.29240	21.49	20.203(25)[36]		
IP3 [eV]	36.841	34.83			

[a] From ref. [32], when not otherwise stated. [b] Relativistic calculation, ref. [34]. [c] Nonrelativistic calculation, ref. [34]. [d] From ref. [35], when not otherwise stated. [e] Ref. [33], ionization to a $6d^87s^2$ state.

Table 3. Properties of solid noble metals.

Property	Ag (R)	Ag (NR)	Ag (exp)	Au (NR)	Au (R)	Au (exp)
a_0 [pm][37]	403	411	409	429	407	408
E_{coh} [eV][37]	3.34	3.01	2.95	3.03	3.96	3.81
B_0 [GPa][37][a]	127	106	100.7	108	182	173.2
$\Delta E_{interband}$ [eV][38]			4	2.38		2.4

[a] The bulk modulus, $B_0 = -V(dp/dV) = [V(d^2U/dV^2)]V_0$.

For the pure metals it is seen from Table 3 that relativistic effects compress gold to the same lattice parameter, a_0, as silver. For the cohesive energy, E_{coh}, and the bulk modulus, B_0, of Ag and Au, the NR values are similar for the two metals while the R values are clearly higher for gold. Thus the same size and stronger bonds for gold, compared to silver, both come from relativity. Finally, the attribution of the yellow color of gold to relativity[3, 39] rests on the result that the relativistic interband energy, $\Delta E_{interband}$, between the top of the 5d band and the Fermi level is close to the experimental value, while the NR interband energy would be much larger.[38] Comparative R/NR calculations of the reflectivity do not seem to exist.

We conclude that relativistic effects are beyond doubt there and influence the properties of gold and its compounds. The main effects at atomic orbital level are the energetic stabilization and radial contraction of the 6s shell and the concomitant destabilization and expansion of the 5d shell.

QED?

How much would these conclusions change, if one goes to still deeper physics, Quantum Electrodynamics (QED), where the main effects are vacuum polarization and self-energy (vacuum fluctuation)? According to the first calculations for the valence electrons of heavy elements,[40] these new effects would only amount to about −1% of the Dirac-level relativistic effects for gold. Thus the conclusions above remain unchanged.

In other words, earlier relativistic quantum chemistry was about "101% right" and including it in chemistry textbooks was quite safe. QED would contribute about −0.026 eV to IP1(Au), compared to relativity which contributes +2.14.[34] Thus the QED terms will be small, but not totally negligible. Indeed, the inclusion of QED may have been "the last train from Physics to Chemistry", at the level of fundamental interactions. The bottleneck for theoretical accuracy on the IP or EA of Au is now in the electron correlation.

Lanthanide Contraction

Lanthanide contraction, in the sense of partial screening of the subsequent 6s valence shell by the filled 4f electrons, was used in the older inorganic literature to explain the properties of gold and other 6th-row elements. An early point made by Kenneth S. Pitzer,[41] by including or omitting the 4f shell in atomic calculations, was that both lanthanide contraction and relativity are needed to reproduce the experimental trend. Their effects are roughly comparable and go in the same direction.

Cesium Auride

Cesium auride was discovered in 1943 by Sommer.[42] A review of the experimentally known alkali metal auride phases was given by Zachwieja.[43] Hensel[44] reviewed the physical properties of CsAu(l) and other liquid ionic alloys. One characteristic feature of them is the deep conductivity minimum at 1:1 stoichiometry (Figure 3). Hensel quotes for the first evidence on auride, Au^-, ions a qualitative observation by Heymann and Weber[46] that sodium alloys with gold dissolve to some extent in molten NaBr. The empirically known high stability of the $6s^2$ electron configuration was brought to the argument by Goodman.[48] Some of these auride species are listed in Table 4. Furthermore, cryptated aurides (Au^- inside a crown ether) are known.[51] Note that bases like alkali metals are able to disproportionate metallic gold to auride aurates, containing Au^{-1} and Au^I ions. An example is $[CsAu]_4[Cs_3AuO_2]$ or $Cs_7Au_5O_2$.[49]

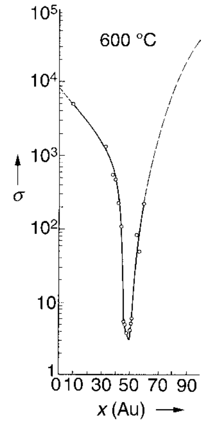

Figure 3. Electric conductivity, σ (in $Ohm^{-1}cm^{-1}$), of liquid cesium–gold alloys at 600 °C (reproduced with permission from ref. [45]; copyright © 1975 Elsevier). x(Au): content of Au in atom %.

Band structure calculations exist on CsAu. A R/NR comparison shows that without relativity the system would be a metal, instead of a semiconductor.[52] Melts of CsAu have also been simulated.[53] Although the results are dependent on the input parameters, it is interesting to note that Au–Au distances of about 300 pm were found.[53a] In contrast, Matsunaga et al. calculated a much longer first Au–Au maximum of the radical distribution function.[53b]

Table 4. Some known aurides.

Auride	Year	Ref.	Comment
RbAu, CsAu	1943	[42]	
M_3AuO; M = K–Cs	1993	[47]	ternary auride oxides
$Rb_5Au_3O_2$, $M_7Au_5O_2$; M = Rb,Cs	2000	[49, 50]	auride aurates
$[N(CH_3)_4]Au$	2002	[51]	first nonmetal auride; isostructural with $N(CH_3)_4Br$.

Parenthetically, in liquid ammonia, also the argentide ion, Ag^-, has been created electrochemically,[54] despite the smaller value of EA(Ag). This system shows a UV band at 382 nm. More generally, in several cases a compound of two metals exhibits a clearly ionic character (with or without electronic conductivity). Hensel quotes as examples Mg_3Bi_2, Li_3Bi, and Li_4Pb.[44]

From CsAu to $BaAu_2$

Knowing that Rb and Cs afford aurides, Goodman asked in 1958 whether their neighbor Ba would do so.[48] The compound $BaAu_2$ mentioned by him had actually been prepared by Biltz and Weibke in 1938.[55] It was characterized as a semiconductor by Shishkin,[56] and has an AlB_2-type crystal structure with Au–Au 277 pm and a yellow color.[57] It has for some reason attracted much less attention than CsAu.

From Au^- to Pt^{2-}?

How about one step to the left, from Au^- to a formal Pt^{2-}? Goodman also mentioned the possible existence of Na_2Pt and BaPt.[48] The most favorable case would be Cs_2Pt, which remains unknown. So does solid BaPt. An attempt to synthesize the latter in the gas phase also failed.[58] Recalling that highly charged anions have been quoted[73] for mercury (e.g. Hg_4^{6-}) despite the low electron affinity of this element, Goodman's proposal for a formal Pt^{2-} or "platinide" ion in a compound would not be absurd.

Closed-Shell Attractions

While dispersion (van der Waals) interactions are well-known, it was only relatively recently that they were identified as the mechanism[29, 30] behind the "aurophilic" or "metallophilic" attractions studied by Schmidbaur[59] and others. Analogous effects between Ag^I ions were discussed by Jansen.[60] Such interactions are found in bridged or unbridged pairs, oligomers, chains,and sheets. They can involve, among others, main-group elements (notably Se and Te), d^{10} ions like Au^I, s^2 ions like In^I and Tl^I, and also d^8 ions like Ir^I, or almost any combination of those above; for a recent summary, see Gade.[61] Note that extremely strong $6s^2$-$6s^2$ attractions were found for the two diatomic systems $AuBa^-$ and $AuHg^-$ by Wesendrup and Schwerdtfeger.[62] The latter has a calculated bond length of about 300 pm, similar to the interauride distances discussed below.

In addition to the dispersion contributions $V(R) = -C_6R^{-6}$, where R is the M–M distance, V the M–M interaction strength, and C_6 the van der Waals coefficient, virtual charge transfer terms were found to play a role near the equilibrium distance, R_e.[63] They decrease exponentially at large values of R. Relativistic effects increased $V(R_e)$ for M = Au by 27 % in one particular calculation on the model $(ClAuPH_3)_2$.[64] The aurophilic interaction thus is not fundamentally relativistic. Electron correlation in a wave-function-based calculation (such as MP2 or CCSD(T)) must be used to reproduce it. Density functional theory (DFT) calculations on the monomers can supply the coefficients C_6 at large R values but cannot be used for a supramolecular approach near R_e because dispersion effects are not built into this theory. One point is that various mechanisms can lead to various power laws, for example, the interaction of two stationary electric dipoles leads to C_3R^{-3} and dispersion effects to C_6R^{-6}. Concerning DFT, treating the two molecules as a "supermolecule" does not even lead to this power law but rather to exponential decay. Also the interaction energy near the van der Waals minimum is unreliable, because the specific form of correlation energy, related to two local dipole moments, is not properly described.

$CsAu \cdot NH_3$

$CsAu \cdot NH_3$ (**1**), was obtained by Mudring et al.[65] by dissolving CsAu in NH_3(l) and subsequently evaporating the ammonia. It shows remarkable features:

1) The crystal is deep blue.
2) The Au^{-I} ions form zig-zag chains with an Au–Au distance of 302 pm (Figure 4). Such an interaction might be called an "auridophilic attraction". Although it takes place between $d^{10}s^2$ Au^{-I} ions, it surprisingly yields a similar distance as the aurophilic attraction between two d^{10} Au^I ions, that could be thought to be smaller. The nature of this effect is not yet clear. Both dispersion effects and net bonding, resulting from partial oxidation from the top of the 6s band, could play a role. The observed Mössbauer isomer shift at gold (CsAu 7.00, RbAu 6.70, **1** 5.96, Au −1.23) does not show a full −1 auride charge and keeps the latter possibility open. A priori, attractive interactions between auride ions in compounds should not be a surprise. Such metallophilic attractions are known between other $d^{10}s^2$ systems. A well-known example is the Tl^I–Tl^I case; here the interaction is rather weak, and indeed the compounds tend to have longer M–M distances.[66] Another example are the smallest nonmetallic mercury clusters, Hg_n. Here the typical Hg–Hg distances are of the order of 350 pm for $n = 2-6$.[67]
3) The crystal contains solvent molecules. Water of crystallization is common, but also examples of "ammonia of crystallization" exist, apart from the well-known inner solvation shell ammonia complexes of transition metals: In his review on Zintl phases, Corbett[68] quotes $Na(NH_3)_n^+$ cations in crystals. A coordination chemistry of the alkali metals with tertiary amines also exists. There are ammonia molecules coordinated to a superoxide anion, O_2^-,[69] and examples of ammonia in alkali metal pnictides are known.[70] Their Cs–N distances are comparable with that in **1** (323 pm). In **1**, each NH_3 binds to two Cs^+ ions, on one side through the nitrogen lone pair (see Figure 4a). The slabs of composition CsAu are intercalated by single NH_3 layers (see Figure 4b). For a discussion on the solvent properties of liquid ammonia, see ref. [71].
4) Thermogravimetrically it was shown that the ammonia is released at 225(5) K, below the boiling point of ammonia (239 K). Here a measurement of the ammonia vapor pressure as a function of temperature would yield its vaporization enthalpy through the Clausius–Clapeyron relation $\Delta H_{vap} = RT^2 d(\ln p)/dT$.
5) Both ^1H and ^{133}Cs NMR and ^{199}Au Mössbauer data were reported. The Cs chemical shift is about 420 ppm from that of 1 M $CsNO_3$(aq) and hence shows no Knight shift typical of metals. The signal has a high-frequency tail, absent in CsAu. The nature of this tail is still not convincingly understood. The proton spectrum suggests hindered rotation of the ammonia molecules about their threefold axes at lower temperatures; at 180 K the line width changes, indicating more free rotation. Here a measurement of the spin–lattice relaxation times, T_1, could yield the activation energies for ammonia rotation. Indeed, this measurement has later been done and yielded an apparent activation energy of 88(3) meV (or 8.5(3) kJ mol^{-1}).[72] This value is about 10 % less than in ammonia.
6) The DFT calculations reported should be acceptable for the other, dominant, bonding contributions but would have a problem with any dispersion-type interactions.

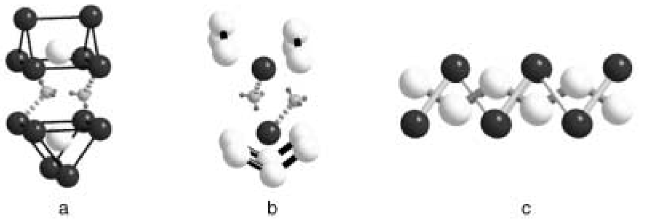

Figure 4. Details of the experimentally determined structure of **1** in the crystal (by courtesy of Dr. Anja-Verena Mudring). a), b) Coordination of the ammonia molecules; c) the gold chains. Large white spheres: Au, large black spheres: Cs, small gray spheres: N.

Ammoniates

In addition to the recent work quoted under point 3 of the list above, readers should be reminded of the thorough investigations of alkali metal, alkaline earth metal, and ammonium halide ammoniates, mostly published about eight decades ago (Table 5). A rule of thumb is that ammoniates are formed by compounds containing cations with a relatively high charge density (e.g., Li, Mg, Ca).[82] The same holds for salts containing easily polarizable anions (e.g., NaI and RbI). Against this background, if we regard gold as a further halogen, compound **1** is a natural member of the series in Table 5, and may only be one particular case in a much larger

Table 5. Ammoniates formed by the alkali metal, alkaline earth metal and ammonium halides. The numbers give the number of NH_3 molecules (from Lagowski[82]).

Cation	Cl^-	Br^-	I^-	Ref.
Li^+	6.5, 5, 4, 3, 2, 1	6.5, 5, 4, 3, 2, 1	7, 5.5, 5, 4, 3, 2, 1	[74, 75]
Na^+	5	5.75, 5.25	6, 4.5	[74]
K^+	–	4	6, 4	[74]
NH_4^+	3	–	4, 3, 2, 1	[76–78]
Rb^+	–	3	6	[74]
Cs^+	–	–	–	[74]
Ca^{2+}	8, 4, 2, 1	8, 6, 2, 1	8, 2, 1	[79]
Sr^{2+}	8, 1	8, 2, 1	8, 6, 2, 1	[80]
Ba^{2+}	8	8, 4, 2, 1	10, 9, 8, 6, 4, 2	[81]

group. Note that gold is the only “halogen” that forms an ammoniate with cesium. The calculated relativistic and nonrelativistic static electric polarizabilities of a free Au^- ion are 93 and 256 a.u., respectively.[83] The largest halide polarizability, that of I^-, is 69 a.u.,[84] not much below the 93 a.u. for auride (1 a.u. of polarizability (α) $\hat{=} 1.6488 \times 10^{-41}$ C^2 m^2 J^{-1} in SI units).

A further question: If we can have NH_3 and H_2O solvent molecules in a crystal, how about HF? Indeed, upon crystallization from anhydrous HF compounds like $Ca(HF)(AsF_6)$ or its Pb and La equivalents were obtained.[85] The HF molecule in these compounds is connected directly to the metal.

Final Comments

Chemistry is a science of analogies and coincidence. Much of the reasoning above was based on seeing the auride ion as a chemical analog to a halogenide, like iodide. Noting that we deal here with very electropositive reagents, one could borrow Feynman’s[86] adage *“There is plenty of room at the bottom”* (with which he meant small devices or “nanotechnology”) to point out the possibility of further surprises at the low end of the electronegativity scale. The serendipitous discovery and investigation of $CsAu \cdot NH_3$ (**1**) at Stuttgart, Bonn, Évora (Portugal), and Santiago de Chile[65] may open a number of doors.[87]

This work was supported by The Academy of Finland. I thank the colleagues who read the manuscript before publication, in particular Prof. J. J. Lagowski for providing Table 5 and Dr. A.-V. Mudring for providing Figure 4. Mr. M. P. Johansson helped to handle the Figure files.

Received: March 4, 2002 [M1554]

---

[1] J. P. Desclaux, P. Pyykkö, *Chem. Phys. Lett.* **1976**, *39*, 300.

[2] P. Pyykkö, *Adv. Quantum Chem.* **1978**, *11*, 353.

[3] P. Pyykkö, J. P. Desclaux, *Acc. Chem. Res.* **1979**, *12*, 276.

[4] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.

[5] The first discussion of the gold maximum appears to be in ref. [3] (Figure 4 ff.). Its existence is evident in the R/NR Hartree–Fock data of J. P. Desclaux, *At. Data Nucl. Data Tables* **1973**, *12*, 311, see pp. 391–404.

[6] a) See Figure 99 in: A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101th ed., Walter de Gruyter, Berlin, **1995**, p. 339; b) see Figure 1-25 in: F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, p. 39.

[7] See Figure 2 in: G. C. Bond, *Gold Bull.* **2001**, *34*, 117.

[8] P. J. Hay, W. R. Wadt, L. R. Kahn, F. W. Bobrowicz, *J. Chem. Phys.* **1978**, *69*, 984.

[9] Y. S. Lee, W. C. Ermler, K. S. Pitzer, A. D. McLean, *J. Chem. Phys.* **1979**, *70*, 288.

[10] U. Kaldor, B. A. Hess, *Chem. Phys. Lett.* **1994**, *230*, 1, and private communication.

[11] P. Schwerdtfeger, J. R. Brown, J. K. Laerdahl, H. Stoll, *J. Chem. Phys.* **2000**, *113*, 7110.

[12] H.-S. Lee, Y.-K. Han, M. C. Kim, C.-B. Bae, Y. S. Lee, *Chem. Phys. Lett.* **1998**, *293*, 97.

[13] B. A. Hess, U. Kaldor, *J. Chem. Phys.* **2000**, *112*, 1809.

[14] G. A. Bishea, M. D. Morse, *J. Chem. Phys.* **1991**, *95*, 5646.

[15] P. Schwerdtfeger, J. S. McFeathers, R. L. Stephens, M. J. Liddell, M. Dolg, B. A. Hess, *Chem. Phys. Lett.* **1994**, *218*, 362. Reported at the REHE conference, de Haan, Belgium, June 10–14, 1993.

[16] D. Schröder, J. Hrušák, I. C. Tornieporth-Oetting, T. M. Klapötke, H. Schwarz, *Angew. Chem.* **1994**, *106*, 223; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 212.

[17] M. Barysz, P. Pyykkö, *Chem. Phys. Lett.* **1998**, 398.

[18] F. Aguirre, J. Husband, C. J. Thompson, R. B. Metz, *Chem. Phys. Lett.* **2000**, *318*, 466.

[19] P. Pyykkö, *J. Am. Chem. Soc.* **1995**, *117*, 2067.

[20] D. Schröder, H. Schwarz, J. Hrušák, P. Pyykkö, *Inorg. Chem.* **1998**, *37*, 624.

[21] S. Seidel, K. Seppelt, *Science* **2000**, *290*, 117.

[22] T. Drews, S. Seidel, K. Seppelt, *Angew. Chem.* **2002**, *114*, 470; *Angew. Chem. Int. Ed.* **2002**, *41*, 454.

[23] W.-P. Hu, C.-H. Huang, *J. Am. Chem. Soc.* **2001**, *123*, 2340.

[24] P. Pyykkö, *Science* **2000**, *290*, 64.

[25] X.-F. Wang, L. Andrews, *J. Am. Chem. Soc.* **2001**, *123*, 12899.

[26] K. Balasubramanian, *Relativistic Effects in Chemistry*, *Part B. Applications*, Wiley, New York, **1997**.

[27] H. Häkkinen, U. Landman, *Phys. Rev. A* **2000**, *62*, R2287. For numerous other calculations, see www.csc.fi/rtam for subjects “gold” or “Au”.

[28] P. Schwerdtfeger, *J. Am. Chem. Soc.* **1989**, *111*, 7261.

[29] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[30] P. Pyykkö, T. Tamm, *Organometallics* **1998**, *17*, 4842.

[31] L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1006.

[32] T. Andersen, H. K. Haugen, H. Hotop, *J. Phys. Chem. Ref. Data* **1999**, *28*, 1511.

[33] E. Eliav, U. Kaldor, P. Schwerdtfeger, B. A. Hess, Y. Ishikawa, *Phys. Rev. Lett.* **1994**, *73*, 3203.

[34] E. Eliav, U. Kaldor, Y. Ishikawa, *Phys. Rev. A* **1994**, *49*, 1724, and private communication. The quoted values include the Breit interaction and were calculated with a larger basis set.

[35] H.-P. Loock, L. M. Beaty, B. Simard, *Phys. Rev. A* **1999**, *59*, 873.

[36] M. Rosberg, J. F. Wyart, *Phys. Scr.* **1997**, *55*, 690.

[37] C. Elsässer, N. Takeuchi, K. M. Ho, C. T. Chan, P. Braun, M. Fähnle, *J. Phys. Condens. Matter* **1990**, *2*, 4371.

[38] a) N. E. Christensen, B. O. Seraphin, *Phys. Rev. B* **1972**, *4*, 3321; b) N. E. Christensen, *Int. J. Quantum Chem.* **1984**, *25*, 233, specifically p. 238.

[39] See p. 583 and reference 359 of ref. [4].

[40] a) P. Pyykkö, M. Tokman, L. N. Labzowsky, *Phys. Rev. A* **1998**, R689; b) L. N. Labzowsky, I. Goidenko, M. Tokman, P. Pyykkö, *Phys. Rev. A* **1999**, 2707.

[41] K. S. Pitzer, *Acc. Chem. Res.* **1979**, *12*, 271. The original paper on this point is P. S. Bagus, Y. S. Lee, K. S. Pitzer, *Chem. Phys. Lett.* **1975**, *33*, 408.

[42] a) A. Sommer, *Nature* **1943**, *152*, 215; b) W. E. Spicer, A. H. Sommer, J. G. White, *Phys. Rev.* **1959**, *115*, 57.

[43] U. Zachwieja in *Gold. Progress in Chemistry, Biochemistry and Technology* (Ed.: H. Schmidbaur), Wiley, New York, **1999**, pp. 495–509.

[44] F. Hensel, *Z. Phys. Chem. N. F.* **1987**, *154*, 201.

[45] H. Hoshino, R. W. Schmutzler, F. Hensel, *Phys. Lett. A* **1975**, *51*, 7.

[46] E. Heymann, H. P. Weber, *Trans. Faraday Soc.* **1938**, 1492.

[47] See a) C. Feldmann, M. Jansen, *Angew. Chem.* **1993**, *105*, 1107; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1049; b) C. Feldmann, M. Jansen, *Z. Anorg. Allg. Chem.* **1995**, *621*, 201; c) M. Jansen, A. V. Mudring in *Gold. Progress in Chemistry, Biochemistry and Technology* (Ed.: H. Schmidbaur), Wiley, New York, **1999**, pp. 747–793.

[48] C. H. L. Goodman, *J. Phys. Chem. Solids* **1958**, *6*, 305.

[49] A.-V. Mudring, M. Jansen, *Angew. Chem.* **2000**, *112*, 3194; *Angew. Chem. Int. Ed.* **2000**, *39*, 3066.

[50] A.-V. Mudring, J. Nuss, U. Wedig, M. Jansen, *J. Solid State Chem.* **2000**, *155*, 29.

[51] P. D. C. Dietzel, M. Jansen, *Chem. Commun.* **2002**, 2208.

[52] a) R. E. Watson, M. Weinert, *Phys. Rev. B* **1994**, *49*, 7148, and references therein. The role of relativistic effects on CsAu was explicitly studied by: b) A. Hasegawa, M. Watabe, *J. Phys. F* **1977**, *7*, 75; c) N. E. Christensen, J. Kollar, *Solid State Commun.* **1983**, *46*, 727.

[53] a) B. J. Costa Cabral, F. M. S. Silva Fernandes, *AIP Conf. Proc.* **1995**, *330*, 129; b) S. Matsunaga, *J. Phys. Soc. Jpn.* **2000**, *69*, 1712.

[54] N. E. Tran, J. J. Lagowski, *Inorg. Chem.* **2001**, *40*, 1067.

[55] W. Biltz, F. Weibke, *Z. Anorg. Allg. Chem.* **1938**, *236*, 12.

[56] Yu. G. Shishkin, *Vestn. Leningr. Univ. Fiz.-Khim.* **1966**, *3*, 58, and references therein; *Chem. Abstr.* **1967**, *66*, 23442. A work function of 4 eV is obtained for $BaAu_2$.

[57] a) G. Bruzzone, *Atti Accad. Naz. Lincei Rend. Cl. Sci. Fis. Mat. Nat.* **1970**, *48*, 235; *Chem. Abstr.* **1970**, *73*, 103005; b) C. B. Alcock, V. P. Itkin, *Bull. Alloy Phase Diagrams* **1986**, *7*, 336; *Chem. Abstr.* **1986**, *106*, 144846.

[58] I. L. Sokol'skaya, *J. Tech. Phys. (Leningrad)* **1957**, *2*, 108; I. L. Sokol'skaya, *Zh. Tekh. Fiz.* **1957**, *27*, 127; *Chem. Abstr.* **1959**, *53*, 2799c.

[59] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11.

[60] M. Jansen, *Angew. Chem.* **1987**, *99*, 1136; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1098.

[61] L. H. Gade, *Angew. Chem.* **2001**, *113*, 3685; *Angew. Chem. Int. Ed.* **2001**, *40*, 3573.

[62] R. Wesendrup, P. Schwerdtfeger, *Angew. Chem.* **2000**, *112*, 938; *Angew. Chem. Int. Ed.* **2000**, *39*, 907.

[63] N. Runeberg, M. Schütz, H.-J. Werner, *J. Chem. Phys.* **1999**, *110*, 7210.

[64] P. Pyykkö, N. Runeberg, F. Mendizabal, *Chem. Eur. J.* **1997**, *3*, 1451.

[65] A.-V. Mudring, M. Jansen, J. Daniels, S. Krämer, M. Mehring, J. P. Prates Ramalho, A. H. Romero, M. Parrinello, *Angew. Chem.* **2002**, *114*, 128; *Angew. Chem. Int. Ed.* **2002**, *41*, 120.

[66] For the latest ab initio treatment, see: P. Pyykkö, M. Straka, T. Tamm, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3441. The C_{2h} symmetric hydride dimer model $(TlH)_2$ and a $(TlCp)_2$ dimer model gave Tl–Tl distances of 322 and 382 pm, respectively; Cp = cyclopentadienyl.

[67] H.-J. Flad, F. Schautz, Y.-X. Wang, M. Dolg, A. Savin, *Eur. Phys. J. D* **1999**, *6*, 243.

[68] J. D. Corbett, *Chem. Rev.* **1985**, *85*, 383.

[69] H. Seyeda, M. Jansen, *J. Chem. Soc. Dalton Trans.* **1998**, 875.

[70] D. Knettel, M. Reil, N. Korber, *Z. Naturforsch.* **2001**, *56*, 965, and references therein.

[71] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, **1984**, pp. 486–489.

[72] S. Krämer, M. Mehring, A.-V. Mudring, M. Jansen, unpublished results.

[73] A. E. Kuznetsov, J. D. Corbett, L.-S. Wang, A. I. Boldyrev, *Angew. Chem.* **2001**, *113*, 3473; *Angew. Chem. Int. Ed.* **2001**, *40*, 3369.

[74] W. Biltz, W. Hansen, *Z. Anorg. Allg. Chem.* **1923**, *127*, 1.

[75] S. Kumao, T. Toriumi, *Bull. Chem. Res. Inst. Non-Aqueous Solutions Tohoku Univ.* **1951**, *1*, 125; *Chem. Abstr.* **1954**, *48*, 7394.

[76] R. Hara, *Jpn. Sci. Rev. Ser. 1* **1944**, *1*, 32; as quoted in ref. [82].

[77] S. Abe, K. Watanabe, R. Hara, *J. Soc. Chem. Ind. Jpn.* **1935**, *38*, 632, Suppl. Binding.

[78] W. Lindberg, as quoted by J. J. Lagowski.[82]

[79] W. Hüttig, *Z. Anorg. Allg. Chem.* **1922**, *123*, 31.

[80] W. Hüttig, *Z. Anorg. Allg. Chem.* **1922**, *124*, 322.

[81] W. Hüttig, W. Martin, *Z. Anorg. Allg. Chem.* **1923**, *125*, 269.

[82] J. J. Lagowski (University of Texas, Austin), February 11, 2002, personal communication.

[83] V. Kellö, M. Urban, A. J. Sadlej, *Chem. Phys. Lett.* **1996**, *253*, 383.

[84] C. Hättig, B. A. Hess, *J. Chem. Phys.* **1998**, *108*, 3863.

[85] M. Tramšek, P. Benkič, A. Turičnik, G. Tavčar, B. Žemva, *J. Fluorine Chem.* **2002**, *114*, 143.

[86] R. P. Feynman, *Engineering and Science (CalTech)*, February **1960**. Available at www.zyvex.com/nanotech/feynman.html.

[87] *Note added in proof (August 20, 2002):* 1) The size of the valence-shell QED effects[40] has been confirmed by Sapirstein and Cheng.[88] 2) Further, recent ammoniates have been reported: $AlX_3 \cdot 5NH_3$, X = Cl–I,[89] $ScCl_3 \cdot NH_3$ and $ScCl_3 \cdot 2NH_3$[90] as well as $MNH_2 \cdot NH_3$, M = K, Cs.[91].

[88] J. Sapirstein, K. T. Cheng, *Phys. Rev. A*, in press.

[89] H. Jacobs, F. O. Schröder, *Z. Anorg. Allg. Chem.* **2002**, *628*, 951.

[90] G. Meyer, D. Klein, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1437.

[91] D. Peters, A. Tenten, H. Jacobs, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1521.