Relativistic effects in gold chemistry. I. Diatomic gold compounds

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Nonrelativistic and relativistic Hartree–Fock (HF) and configuration interaction (CI) calculations have been performed in order to analyze the relativistic and correlation effects in various diatomic gold compounds. It is found that relativistic effects reverse the trend in most molecular properties down the group (11). The consequences for gold chemistry are described. Relativistic bond stabilizations or destabilizations are dependent on the electronegativity of the ligand, showing the largest bond destabilization for AuF (86 kJ/mol at the CI level) and the largest stabilization for AuLi (− 174 kJ/mol). Relativistic bond contractions lie between 1.09 (AuH^+) and 0.16 Å (AuF). Relativistic effects of various other properties are discussed. A number of as yet unmeasured spectroscopic properties, such as bondlengths (r_e), dissociation energies (D_e), force constants (k_e), and dipole moments (μ_e), are predicted.

I. INTRODUCTION

A few diatomic gold compounds have been studied theoretically in the past,[1–3] mainly Au_2 and AuH, primarily to investigate the effects of relativity on the AuX (X = Au, H) bond. Other compounds have not been studied extensively. For instance, the bond distances in the diatomic gold halogenides and chalcogenides are unknown. Many problems in gold chemistry remain unsolved, e.g., the origin of the relativistic bond stabilization or destabilization (some aspects are given in Ref. 2), or the reason for the greater stability of higher oxidation states in inorganic gold compounds in contrast to the chemistry of silver or copper. In contrast to inorganic gold chemistry, organo Au(III) compounds of the type AuR_3 (R = alkyl, aryl) are very reactive[4] (e.g., $AuMe_3$ (Me = CH_3) decomposes at − 40 °C[5]), whereas organo Au(I) compounds of the type AuR_2^- are more stable.[4] Organo Au(III) compounds can be stabilized only by introducing electronegative ligands, e.g., compounds of the form R_2AuX (R = alkyl, aryl; X = halogen) are known to be stable.[4] This may be compared to Tl, Pb, and Bi chemistry, where we find exactly the reverse trend, e.g., Tl(I) and Pb(II) alkyls are unknown[6,7] and BiF_5 is one of the most powerful fluorinating agents.[8]

It has been known for a long time that chemical and physical properties of Au compounds are quite different to those of copper and silver. This is often called the "Au anomaly."[9] For example, the most common coordination number of Au(I) is two, whereas Ag(I) and Cu(I) tend to form complexes with higher coordination numbers.[4] The oxidation state III is most important only for Au compounds and even oxidation numbers up to VII have been reported recently.[10] The same differences are found for the chemistry of mercury compared to cadmium and zinc, e.g., the unique stability of the Hg_2^{2+} ion,[9] the fact that mercury is a liquid at room temperature or the strikingly high superconducting transition temperature of mercury ($T_c = 4.15$ K) compared to cadmium ($T_c = 0.52$ K) or zinc ($T_c = 0.85$ K).[11,12] What makes the heavy elements so different from their lighter group members?

Most inorganic textbooks explain the stability of higher oxidation states in Au compounds by larger 5*d* contributions caused from the lanthanide contraction; because of the reduced screening of the nucleus by the 4*f* electrons, the 6*s* orbital is contracted.[4] This contraction leads to the chemical stability of Au, contributes to its noble character and is made responsible for the shorter bond distances found in gold compounds, Fig. 1. However, the lanthanide contraction cannot explain the expansion of the 5*d* and (to a lesser ex-

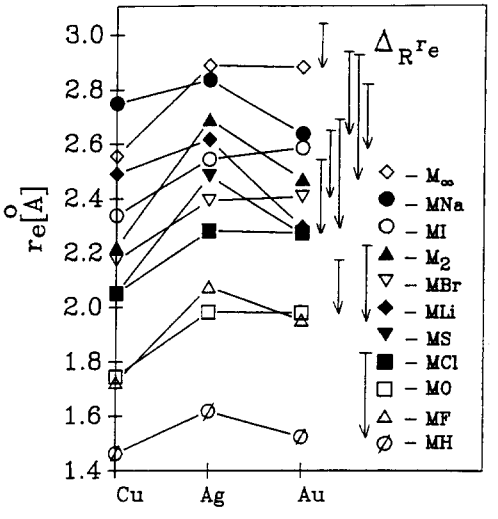

FIG. 1. Experimental and CI bond distances for various group(11) transition metal compounds in Å. The values are taken from Refs. 14 and 15 and from Table I. The vertical lines for $\Delta_R r_e$ ($R \leftarrow NR$) represent the calculated HF relativistic bond contraction for Au.

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tent) 6*p* orbitals. It has been known since the beginning of the seventies,[2] that the large 6*s* contraction and stabilization (inert 6*s* orbital) is only partially caused by the lanthanide contraction, a large contribution being due to "direct" relativistic effects.[9,13]

The chemically inert character of the 6*s* electrons was first discussed by Sidgwick in 1933[16] and in more detail later by Nyholm in 1961.[17] Although the foundations of relativistic quantum mechanics were laid in the late twenties by Dirac, the dominant relativistic contributions to this phenomenon were recognized only about fifty years later[9] (Fig. 2). Due to relativistic effects, the 6*s* orbital is strongly contracted (by about 17%), whereas the 5*d* orbitals slightly expand. Taking the orbital energies of Au, we get the schematic picture as shown in Fig. 3. We should comment on some important facts. First, the lanthanide contraction, too, contributes to the contraction of the 6*s* orbital.[9] Second, the relativistic 6*s* contraction is *not* an indirect effect due to the orthogonality restriction to the relativistically contracted inner shells as is often proposed, but results from the direct action of the relativistic perturbation operator on the inner tail of the valence orbital.[13] Third, fine-structure effects are important for the 5*d* and 6*p* shell; the corresponding splitting (mainly spin–orbit coupling) is about 0.5 eV for the 6*p* orbital (Au $^2P_{1/2};^2P_{3/2}$) and 1.5 eV for the 5*d* orbital (Au $^2D_{1/2};^2D_{3/2}$).[18] Such effects are certainly important for excited states of Au compounds and possibly also in CI treatments.

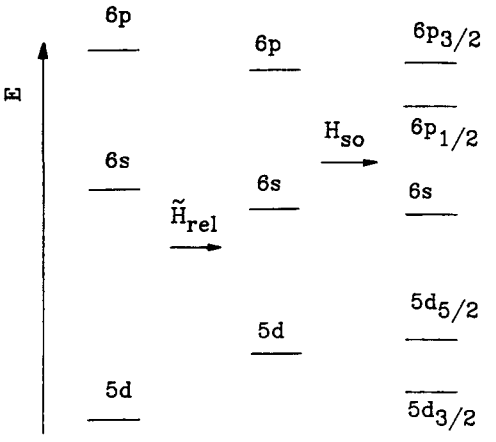

FIG. 3. Relativistic effects on Au orbital energies. The HF and DF values are calculated with programs MCHF (Ref. 19) and MCDF (Ref. 20). $\tilde{H}_{\rm rel}$: spin–orbit averaged relativistic perturbation operator. $H_{\rm SO}$: spin–orbit operator (Ref. 21).

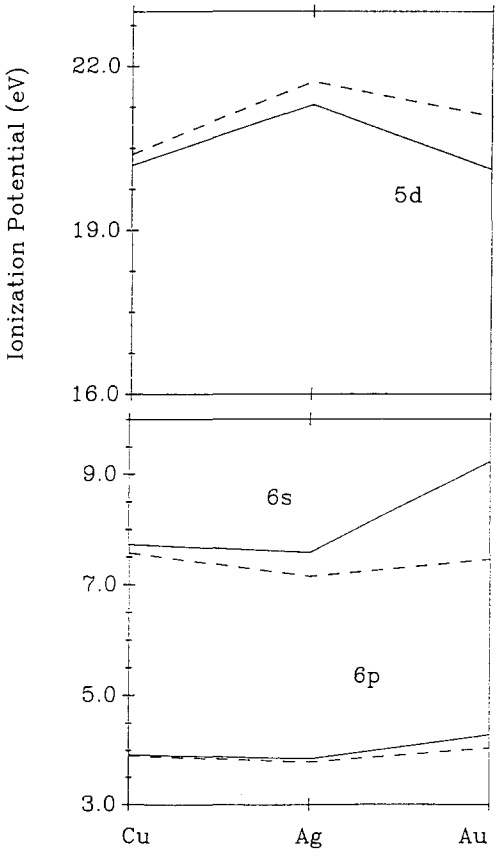

FIG. 2. Relativistic and nonrelativistic ionization potentials of gold in eV. —exp. (Ref. 18); --NR [exp. plus Δ_RIP from Table VIII (Refs. 19 and 20)]. 6*p*: Au $^2P(5d^{10}6p^1)\rightarrow Au^+\ ^1S(5d^{10})$; 6*s*: Au $^2S(5d^{10}6s^1)\rightarrow Au^+\ ^1S(5d^{10})$; 5*d*: $Au^+\ ^1S(5d^{10})\rightarrow Au^{2+}\ ^2D(5d^9)$.

Relativistic SCF calculations for molecules containing heavy elements are extremely time-consuming. The pseudopotential or effective core potential method (PP) is a fast method that can describe molecular properties almost as accurately as all-electron calculations. Furthermore, relativistic effects can easily be included either in a spin–orbit averaged way (one-component PP) or by including spin–orbit coupling (two-component PP). Such methods have been reviewed several times and have been used with remarkable success, yielding molecular spectroscopic properties for a large number of molecules.[22] In this paper we use highly accurate pseudopotentials for gold, constructed by a multielectron fit procedure,[23] which effectively improves the quality of the pertinent approximations. The procedure is described in Sec. III.

In the first paper of this series on relativistic studies in gold chemistry[24] we give the results of HF and CI calculations on various diatomic gold compounds: AuH^+ ($^2\Sigma^+$), AuH ($^1\Sigma^+$), AuH^- ($^2\Sigma^+$), AuLi ($^1\Sigma^+$), AuO ($^2\Pi,^2\Sigma^-$), AuF ($^1\Sigma^+$), AuNa ($^1\Sigma^+$), AuS ($^2\Pi,^2\Sigma^-$), AuCl ($^1\Sigma^+$), AuBr ($^1\Sigma^+$), AuI ($^1\Sigma^+$), Au_2^+ ($^2\Sigma_g^+$), Au_2 ($^1\Sigma_g^+$), and Au_2^- ($^2\Sigma_u^+$). For comparison with silver and copper compounds, we also performed calculations on CuLi ($^1\Sigma^+$), CuNa ($^1\Sigma^+$), AgLi ($^2\Sigma^+$), AgF ($^1\Sigma^+$), AgNa ($^1\Sigma^+$), AgS ($^2\Pi$), and AgCl ($^1\Sigma^+$). To guarantee results comparable to those of all-electron self-consistent field (SCF) calculations, energy adjusted nonrelativistic (NRPP) and spin–orbit averaged relativistic pseudopotentials (ARPP) have been used for gold. In addition, correlation is taken into account at the ARPP level of approximation, using CISD procedures (configuration interaction with single and double excitations, corrected by size-consistency effects CISD/SC), and CEPA-1 procedures (coupled electron pair approximation).

We define the relativistic effect Δ_R for an atomic or molecular property $\Delta_R\mathbf{P}$ as $\Delta_R\mathbf{P} = \mathbf{P}^{\rm NR} - \mathbf{P}^R$, where $\mathbf{P}^{\rm NR}$ is the property derived from a nonrelativistic (NR) calculation and $\mathbf{P}^R$ is the one derived from a relativistic (R) calcu-

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lation. $\Delta_R P$ is discussed only at the Hartree–Fock (HF) level of the theory, because accurate relativistic CI calculations are very time consuming. It will be shown that the important trends in relativistic effects presented in this paper are in agreement with experimental observations. In addition, we present nonrelativistic CI calculations for AuLi, AuH, and AuF.

II. RESULTS AND DISCUSSION

A. Relativistic bond contractions

As is well known from pioneering calculations of Desclaux and Pyykkö,[2,9] the stable AuX (X = any ligand) bonds are shortened by relativistic effects (while the relatively unstable Tl_2 and TlH^+ molecules are expanded by relativistic effects[22,25]). This explains the bond length behavior of the compounds in the copper group (Fig. 1). The bond length contraction is related to the valence *s*-orbital contraction,[26] but may also be explained along alternative lines.[27] The calculated bond distances are shown together with other

TABLE I. (A) Bond distances r_e (Å), dissociation energies D_e (kJ/mol), force constants k_e (mdyn/Å = N/cm), and harmonic vibrational frequencies ν_e [cm^{-1}] for diatomic gold compounds. Experimental data from Ref. 14. ARPP*: ARPPs are also used for Br and I. CI and CISC are the abbreviations for CISD and CISD/SC. (B) Bond distances r_e (Å), dissociation energies D_e (kJ/mol), force constants k_e (mdyn/Å), and dipole moments μ_e [D] of Cu and Ag diatomics from all-electron SCF calculations and of AuO and AuS from ARPP/CISC calculations. The term values T_e are given in eV. An asterisk indicates the first excited $^2\Sigma^-$ state.

(A)		r_e	D_e	k_e	ν_e
AuF	NRPP	2.174	163.1	1.839	424
	ARPP	2.010	88.6	2.530	498
	CI	1.980	166.7	2.665	511
	CISC	1.978	215.5	2.645	509
	CEPA-1	1.991	241.8	2.430	488
AuO	NRPP	2.225	− 5.6	1.622	431
	ARPP	2.012	34.6	2.422	527
	CI	1.960	52.5	2.318	516
	CISC	1.953	108.0	2.321	516
	CEPA-1	1.946	146.5	2.153	497
	exp.		225		
AuCl	NRPP	2.541	217.9	1.220	264
	ARPP	2.333	160.7	1.870	327
	CI	2.280	176.8	2.124	348
	CISC	2.274	220.7	2.131	349
	CEPA-1	2.278	242.8	2.064	383
	exp.		(340)	2.564	383
AuBr	NRPP	2.647	202.7	1.182	189
	ARPP	2.448	157.2	1.770	231
	ARPP*	2.444	154.1	1.723	228
	CI	2.409	189.3	1.924	241
	CISC	2.408	224.9	1.910	240
	CEPA-1	2.402	225.4	1.770	231
AuI	NRPP	2.824	191.4	1.016	149
	ARPP	2.616	152.4	1.605	188
	ARPP*	2.616	138.9	1.533	184
	CI	2.586	171.8	1.596	188
	CISC	2.587	206.2	1.684	193
	CEPA-1	2.580	208.1	1.604	188

TABLE I (*continued*).

(A)		r_e	D_e	k_e	ν_e
Au_2^+	NRPP	3.276	103.7	0.191	57
	ARPP	2.859	120.4	0.528	95
	CI	2.728	97.2	0.780	116
	CISC	2.706	143.6	0.853	121
	CEPA-1	2.697	168.7	0.902	125
Au_2	NRPP	2.930	30.6	0.572	99
	ARPP	2.624	67.0	1.366	153
	CI	2.544	80.5	1.627	167
	CISC	2.537	137.9	1.737	173
	CEPA-1	2.540	178.9	1.674	170
	exp.	2.472	222	2.114	191
Au_2	NRPP	3.137	46.8	0.232	63
	ARPP	2.798	76.6	0.600	102
	CI	2.679	53.9	0.923	126
	CISC	2.667	110.4	0.979	129
	CEPA-1	2.663	157.6	0.994	131
AuS	NRPP	2.575	86.8	1.124	263
	ARPP	2.329	78.6	1.815	335
	CI	2.268	110.3	2.013	353
	CISC	2.270	157.8	2.024	353
	CEPA-1	2.260	186.1	1.983	350
	exp.		250		
AuH^+	NRPP	2.636	6.9	0.055	305
	ARPP	1.549	43.4	2.665	2124
	CI	1.499	144.0	3.192	2324
	CISC	1.501	166.4	3.157	2312
	CEPA-1	1.513	176.4	2.824	2187
AuH	NRPP	1.831	92.3	1.260	1461
	ARPP	1.578	152.7	2.510	2061
	CI	1.509	260.1	3.081	2284
	CISC	1.504	285.5	3.092	2288
	CEPA-1	1.512	299.5	3.002	2254
	exp.	1.524	311	3.139	2305
AuH^-	NRPP	1.931	110.5	0.781	1150
	ARPP	1.668	109.4	1.580	1636
	CI	1.603	160.5	1.930	1808
	CISC	1.602	166.9	1.927	1807
	CEPA-1	1.614	191.3	1.770	1731
AuLi	NRPP	2.691	38.8	0.338	291
	ARPP	2.381	121.1	0.670	410
	CI	2.301	237.6	0.778	442
	CISC	2.295	254.9	0.798	447
	exp.		281	1.90	705
AuNa	NRPP	2.942	25.5	0.293	155
	ARPP	2.692	92.5	0.551	213
	CI	2.643	195.3	0.656	232
	CISC	2.638	211.1	0.672	235
	exp.		210		

(B)	r_e	D_e	k_e	μ_e	
CuLi	2.491	78.8	0.370	− 3.057	
CuNa	2.750	65.1	0.322	− 3.868	
AgLi	2.617	39.8	0.281	− 1.814	
AgF HF	2.081	198.8	1.880	8.290	
AgNa	2.836	34.0	0.311	− 2.645	
AgS	2.484	28.5	0.981	8.626	
AgCl	2.439	245.4	1.326	8.745	
AuO	1.946	146.5	2.153	3.41	
AuO* CI	1.861	· · ·	3.220	2.62	$T_e = 1.340$
AuS CI	2.260	186.1	1.983	2.79	
AuS*	2.278	· · ·	1.761	3.83	$T_e = 1.787$

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TABLE II. Relativistic effects in diatomic gold compounds. $\Delta_R r_e$ in Å, $\Delta_R D_e$ in kJ/mol, $\Delta_R k_e$ in mdyn/Å.

	$\Delta_R r_e$	$\Delta_R D_e$	$\Delta_R k_e$
AuF	0.164	+ 74.5	− 0.70
AuO	0.213	− 29.0	− 0.80
AuCl	0.208	+ 57.1	− 0.65
AuBr	0.199	+ 45.5	− 0.59
AuI	0.208	+ 39.0	− 0.59
Au_2^+	0.417	− 16.7	− 0.34
Au_2	0.306	− 36.4	− 0.79
Au_2^-	0.339	− 29.8	− 0.37
AuS	0.246	+ 8.2	− 0.69
AuH^+	1.087	− 36.6	− 2.61
AuH	0.253	− 60.4	− 1.25
AuH^-	0.263	+ 1.1	− 0.80
AuLi	0.310	− 82.3	− 0.33
AuNa	0.250	− 67.0	− 0.26

molecular properties in Table I. The relativistic effects are listed separately in Table II. In nearly all cases the relativistic bond contraction $\Delta_R r_e$ is smaller (< 0.25 Å) than the relativistic 6*s* orbital contraction, which is 0.34 or 0.26 Å taking the expectation value of *r*, or the outermost maximum of the radial 6*s* density, respectively, as a measure for the orbital contraction. The only exception is AuH^+ where relativity causes a very large reduction of r_e due to the extreme flatness of the nonrelativistic potential curve. It is interesting to note that $\Delta_R r_e$ decreases as the electronegativity of the ligand X, EN_X, increases (Fig. 4.).

To explain this result, we consider two extreme ionic cases: Au^+X^-, which describes ionic systems such as the gold halogenides, and Au^-X^+, which is found, e.g., in the gold–alkali compounds. The relativistic 5*d* expansion leads to a small increase in the ionic Au^+ radius whereas the 6*s* contraction leads to a strong decrease of the atomic Au and ionic Au^- radii. Hence, in an ideal Au^+X^- system we would expect a small relativistic increase in the bond length, whereas for an ideal Au^-X^+ system we expect a strong bond contraction. This is exactly the tendency shown in Fig. 4.

The relativistic bond contraction in AuLi is remarkably large, and we expect drastic changes due to relativity in the chemistry of such species.

B. Relativistic effects on dissociation energies

How is the stability of Au(I) compounds influenced by relativistic effects? From the Mulliken definition of the electronegativity, EN = 0.18 (IP + EA), where IP and EA are the ionization potential and electron affinity in eV, respectively, we obtain from HF and Dirac Fock (DF) calculations[19,20] $\Delta_R EN_{Au} = -0.4$. Hence, relativistic effects increase the electronegativity of Au. The estimated Pauling electronegativity is 2.4,[28] the nonrelativisic value would therefore be 2.0. For ligands X and $EN_X > EN_{Au}$ the ionic contribution to the bond is reduced by relativistic effects. We expect a relativistic destabilization of the AuX bond, since the promotion energy of a 6*s* electron is larger in the relativistic case. For ligands with $EN_X < EN_{Au}$ the ionic contribution to the bond is increased and we expect a stabilization of the AuX bond by relativistic effects. Although this ionic viewpoint neglects the covalent contributions, it explains the earlier findings, namely a stabilization of about 0.6 eV for AuH[29] but a destabilization of the same amount for AuCl.[30]

The relativistic change in the dissociation energy $\Delta_R D_e$ (Table II) as a function of the ligand electronegativity is shown in Fig. 5. The S-shape behavior results from the limitation of the strength of an ideal ionic interaction: $\Delta_R D_e$ is limited by − IP(Au), if gold is the electropositive ligand; and by + EA(Au), if gold is the electronegative one. At the HF level we get $\Delta_R IP = -169.6$ kJ/mol and $\Delta_R EA = -55.0$ kJ/mol, respectively.[19,20]

To analyze the stability behavior of the diatomic gold compounds in more detail, we present in Fig. 6 the nonrelativistic and relativistic valence MO pictures of AuLi and AuF. In the case of AuLi, the electron transfer from Li to Au increases the interelectronic repulsion on the gold atom, so that the 5*d* and 6*d* levels are raised. The doubly occupied

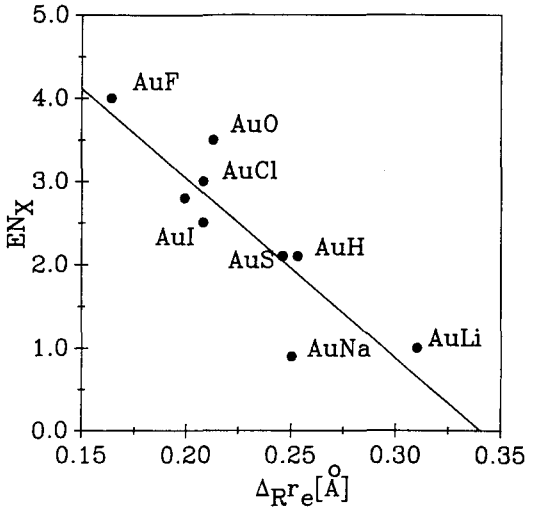

FIG. 4. Relativistic bond contractions $\Delta_R r_e$ of various AuX compounds in Å. EN_X: Pauling electronegativity of the ligand X (Ref. 28).

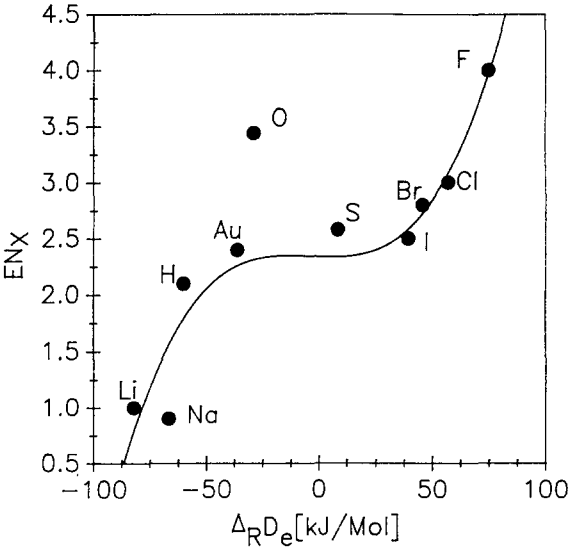

FIG. 5. Relativistic AuX bond (de)stabilization $\Delta_R D_e$ in kJ/mol. EN_x: Pauling electronegativity of the ligand X in AuX (Ref. 28).

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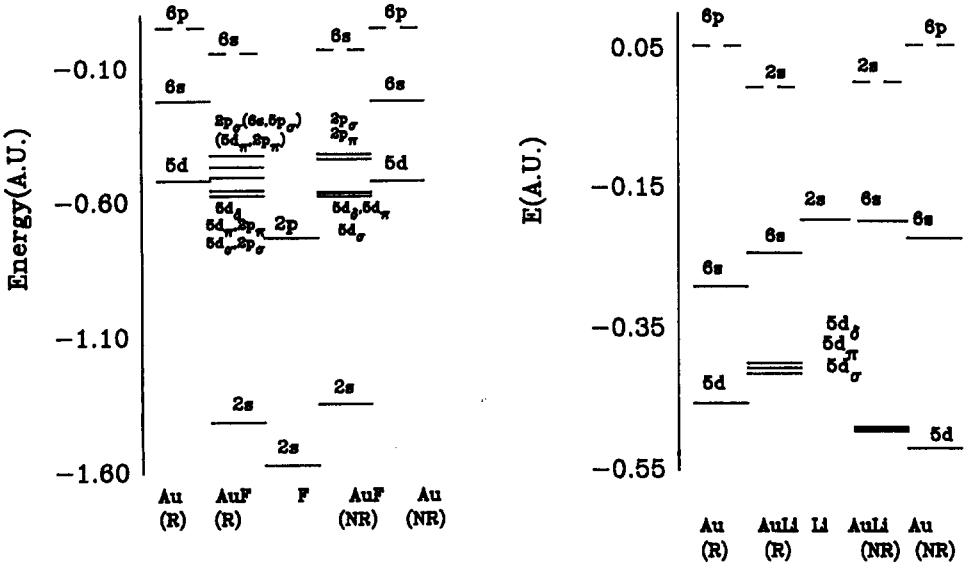

FIG. 6. MO schemes for AuLi and AuF. The orbital energies are given in a.u. The dominant AO contributions to the MOs are indicated.

Au(6*s*)-type MO effectively shields the Au(5*d*) orbitals so that the molecular field splitting remains small. The relativistic stabilization of the Au(6*s*) orbital stabilizes the ionic molecules with Au^-, thereby increasing D_e, that is $\Delta_R D_e < 0$. In the case of AuF on the other hand, the electron transfer from Au to F is impeded by the relativistic Au(6*s*) stabilization, thereby decreasing the bond energy between F^- and Au^+, $\Delta_R D_e > 0$. This is shown schematically in Fig. 7. The reduced electronic charge on Au stabilizes the 5*d* levels. Nevertheless, they interact much more strongly with the ligand orbitals than in AuLi. The F($2p_\sigma$) and F($2p_\pi$) overlap with Au(5*d*) is much better in the relativistic regime, because the 5*d* core AOs are relativistically expanded. This explains the bond stability trends of the diatomic group(11) compounds shown in Fig. 8. Only very few experimental data for diatomic gold compounds are available. Theoretical investigations of copper and silver compounds are not very extensive in the literature.[32] We have, therefore, performed HF calculations on CuLi, CuNa, CuCl, AgLi, AgNa, AgS, and AgCl. The results are given in Table I(B) (for details of the basis sets used see Sec. III). The SCF data for the copper and silver dimers and hydrides as well as for CuCl have been taken from Ref. 15. Experimental and CI results reflect the same behavior as that shown in Fig. 8. For example, the few known experimental dissociation energies (in kJ/mol) are: CuH 266, AgH 220, AuH 311; Cu_2 196, Ag_2 160, Au_2 222.[14] AuO and AuS are Au(II) compounds with an open $^2\Pi$ shell and do not fit into this scheme. For these two molecules we have also calculated the first excited $^2\Sigma^-$ state [see Table I(B)].

Spin–orbit effects may be important in gold compounds containing bromine or iodine as a ligand. For σ bonds we expect that the atomic spin–orbit stabilization Δ_A is much larger than the corresponding stabilisations at the molecular level Δ_M, i.e., $\Delta_A^{SO} \gg \Delta_M^{SO}$. This has been shown for the dimers

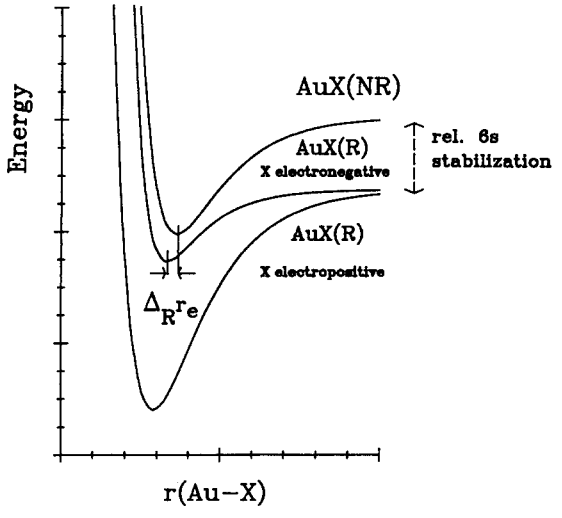

FIG. 7. Schematic representation of the AuX dissociation curve for electronegative and electropositive gold ligands.

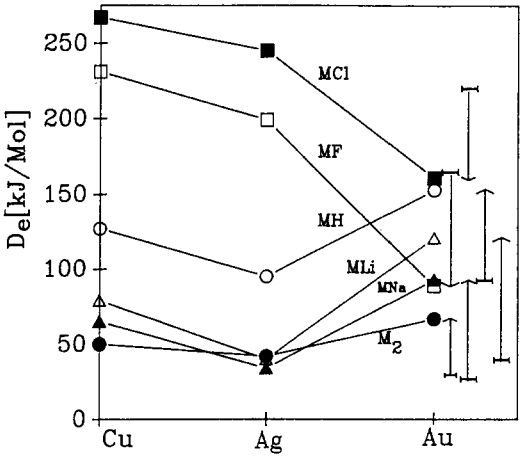

FIG. 8. HF dissociation energies D_e in kJ/mol. The vertical lines for $\Delta_R D_e$ is indicated by $R \leftarrow NR$; ↑ means $\Delta_R D_e < 0$ and ↓ means $\Delta_R D_e > 0$.

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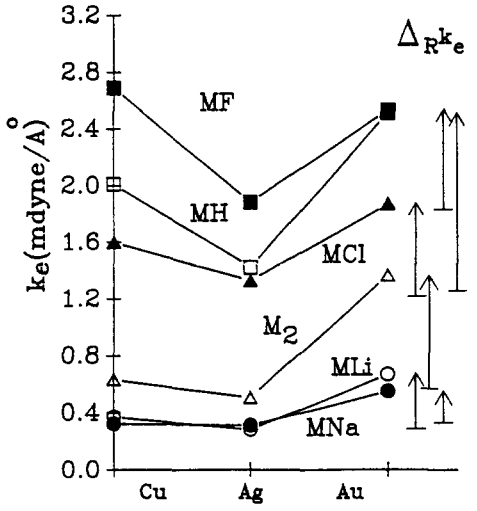

FIG. 9. HF force constants k_e in mdyn/Å. The vertical lines for $\Delta_R k_e$ is indicated by $R \leftarrow$NR.

and hydrides of bromine and iodine.[61] Hence, the spin–orbit corrected D_e for AuBr and AuI is expected to be lower compared to the averaged relativistic case, i.e., $\Delta_R^{SO} D_e > \Delta_R D_e$. Taking the HF values $\Delta_A^{SO}(\mathrm{Br}) = 14$ kJ/mol and $\Delta_A^{SO}(\mathrm{I}) = 30$ kJ/mol[61] we obtain the atomic spin–orbit corrected relativistic bond destabilizations $\Delta_R^{SO} D_e(\mathrm{AuBr}) = 59$ kJ/mol and $\Delta_R^{SO} D_e(\mathrm{AuI}) = 69$ kJ/mol. Because $\Delta_M > 0$, the spin–orbit corrected HF $\Delta_R D_e$ are expected to be smaller than these values. Hence the trend shown in Fig. 5. will not be changed by spin–orbit effects.

The adiabatic ionization energies of the molecules AuH, AuH^-, Au_2, and Au_2^- are listed in Table III. Experimental values are not available. Large relativistic effects of about 2 eV are observed for the neutral species, which are related to the relativistic Au(6*s*)-AO stabilization. The relativistic modification of the electron affinities (i.e., IPs of Au_2^- and AuH^-) are much smaller, because the LUMO has less Au(6*s*) character.

C. Relativistic effects on force constants

Calculated force constants of copper, silver and gold compounds are shown in Fig. 9. In all cases, k_e shows a relativistic increase ($\Delta_R k_e < 0$), even if the bond is energetically destabilized, for instance in the case of the gold halogenides. This trend in force constants was pointed out earlier by one of us[33] and turns out to be clearly a relativistic effect. The nonmonotonic behavior of k_e in group(11) is also found in the relatively few known experimental data (in mdyn/Å): CuH 2.202, AgH 1.822, AuH 3.002; CuCl 2.309, AgCl 1.831, AuCl 2.563; Cu_2 1.297, Ag_2 1.176, Au_2 2.114.[14] Puddephatt suggested[4] that the decrease in the force constant along the series Au > Cu > Ag reflects the degree of covalence in the MX bond (M = Cu,Ag,Au). However, AuLi is more ionic at the relativistic level compared with the nonrelativistic case, but a relativistic increase of the force constant was found in all cases. As pointed out recently, a strong relativistic increase in the force constants of gold compounds is also found in frozen 5*d*-core calculations.[34] The general increase in k_e is consistent with the general relativistic bond length contraction for gold compounds. Hence it may be a "topological" effect of the potential curves: a decrease in bond length results in a steeper potential curve, even if the well depth is reduced, and, therefore, increases the force constant. The largest increases in force constants are found for AuH and Au_2 (disregarding the special case AuH^+), i.e., for the molecules which are regarded as covalent. For the more ionic species (e.g., AuF and AuLi) the increase of the force constants is smaller.

TABLE III. Adiabatic ionization energies (eV) for AuH, AuH^-, Au_2, and Au_2^-.

	NRPP	ARPP	CISD	CISD/SC	CEPA-1
Au_2	5.18	7.12	8.15	8.42	8.55
Au_2^-	0.28	0.75	1.15	1.32	1.54
AuH	6.83	8.81	9.58	9.75	9.84
AuH^-	0.29	0.20	0.35	0.41	0.49

D. Relativistic effects on dipole moments

The dipole moments (reference direction Au^+X^-) decrease in all cases by nearly the same amount of ~2–3 D (see Table IV). This is explained by the relativistic increase in the electronegativity of gold. The relativistic change in μ_e re-

TABLE IV. Relativistic and correlation effects on dipole moments. μ_e values in debye, a minus sign indicates the negative charge on Au. $\partial\mu/\partial r$ in D/Å [Eq. (2)].

	μ_e^{NR}	μ_e^R	$\Delta_R\mu_e$	$\Delta_R\mu(r_e^{NR})$	$\Delta^{bond}\mu^R$	$\partial\mu^{NR}/\partial r$	$\partial\mu^R/\partial r$	μ_e^{CEPA-1}
AuF	8.49	6.60	1.89	0.70	1.19	5.5	5.6	4.84
AuO	8.08	5.53	2.54	1.68	0.87	5.7	4.1	3.40
AuCl	8.90	6.22	2.68	1.68	1.00	5.1	4.6	4.41
AuBr	8.33	5.89	2.43	1.54	0.90	4.6	4.2	3.94
AuI	8.37	5.40	2.97	2.19	0.78	4.4	3.2	3.31
AuS	7.78	4.69	3.10	2.92	0.17	2.5	3.9	2.79
AuH	5.16	2.69	2.47	1.95	0.52	2.5	1.9	0.58
AuLi	−2.55	−5.44	2.89	3.61	−0.72	−0.4	−2.3	−6.24
AuNa	−3.38	−6.73	3.36	4.01	−0.66	−1.0	−2.6	−7.89

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sults from the action of the relativistic perturbation operator on the electronic wave function at the internuclear distance r_e^{NR}, and also from the relativistic bond contraction:

$$\Delta_R\mu_e = \Delta_R\mu(r_e^{NR}) + \Delta^{Bond}\mu^R ,$$
$$\Delta^{Bond}\mu^R = \mu^R(r_e^{NR}) - \mu^R(r_e^R) . \quad (1)$$

The different contributions to Eq. (1) are listed in Table IV. Except for AuF, $\Delta_R\mu(r_e^{NR})$ is the dominant contribution, but the bond contraction term $\Delta^{Bond}\mu^R$ is not negligible. In general, $\Delta_R\mu(r_e^{NR})$ increases from the electronegative to the electropositive ligands. As pointed out above, molecular relativistic effects are smaller for Au^+X^- than for Au^-X^+ compounds (except in the case of D_e, which is the difference between the molecule and the separated atoms). If it is assumed that the dipole moment varies linearly with the Au–X bond distance we obtain

$$\Delta^{Bond}\mu^R = \frac{\partial\mu^R}{\partial r}\Delta_R r_e . \quad (2)$$

AuF has a small relativistic bond contraction but a very large value in the dipole moment derivative (Tables II and IV) resulting in a large value for $\Delta^{Bond}\mu^R$. The value of $\partial\mu^R/\partial r$ of AuX decreases significantly for decreasing EN of the ligand X. Therefore $\Delta^{Bond}\mu^R$ decreases, too. This decrease happens to compensate the increase of $\Delta_R\mu(r_e^{NR})$ so that $\Delta_R\mu_e$ does not vary very much with varying ligand electronegativity. The mentioned trend of $\partial\mu^R/\partial r$ should also show up in the infrared intensities of gold compounds. According to the electronegativities, or from the approximation of fixed charges ($\partial\mu/\partial r = q$, the charge of the dipole) we expect a decrease of the atomic charge on Au in the gold halides from fluorine to iodine. Indeed, a Mulliken population analysis yields the following gross atomic charges: F -0.65, Cl -0.45, Br -0.42, I -0.32. One may ask about relativistic effects in infrared intensities and compare relativistic and nonrelativistic dipole moment derivatives.[35,36] The data in Table IV show a relativistic decrease in $\partial\mu/\partial r$ except for AuS and AuF.

E. Relativistic effects—physics and chemistry of gold

1. Au_n compounds

We can now discuss the significance of relativistic effects in the physics and chemistry of gold. Let us begin with gold metal (Au_∞). Others have shown that the yellow color of gold is a relativistic effect, "nonrelativistic" gold would look like silver.[38] However, there are other physical properties of gold which are strongly influenced by relativistic effects. Gold, silver, and copper form solids with closed packed face centered cubic structures (fcc). The calculated bond contraction in the solid is 0.16 Å (Ref. 39 and Fig. 1) which is about 50% of that in Au_2. Hence, due to the relativistic bond contraction, the density of metallic gold increases by 18%. This contraction shows up in the relatively small atomic volume of gold compared to copper and silver (in cm^3/mol)[11]: Cu 7.12, Ag 10.28, Au 10.21 (12.1 at the nonrelativistic level). The large relativistic bond stabilization in Au_2 is reflected in the sequence of cohesive energies of the metals (in kJ/mol): Cu 330, Ag 280, Au 370.[11] This results in a relatively high melting point for gold compared to copper or silver (in °C): Cu 1083, Ag 961, Au 1064.[11] The same trend is seen in the boiling points (in °C): Cu 2567, Ag 2212, Au 3080.[11] The increase in the force constant of Au_2 is probably also found in metallic gold, where we expect a shift in the phonon frequencies to higher values. It is well known that the relativistic effects are important in the band theory of solids containing heavy elements.[40] Kupratakuln and Fletcher showed that the neck radius of the Fermi surface in gold is smaller and less spherical in the relativistic than in the nonrelativistic regime.[38] The electron–phonon interaction[41] is therefore expected to change relativistically. This is probably reflected in the series of specific resistivities ρ (in 10^{-8} Ω m; 20 °C): Cu 1.72, Ag 1.62, Au 2.4.[11] Since superconductivity may be described by phonon exchanges between electrons at the Fermi surface leading to an attractive interaction between two electrons (Cooper pairs) we also expect a relativistic change in the superconducting transition temperature of gold compounds.[12] According to the Wiedemann–Franz law the thermal conductivity c is related to the specific resistivity by $c = L.T/\rho$, where the Lorentz constant L lies between 2.2 and 2.7×10^8 W Ω K^{-3} for most metals ($L = 2.30 \pm 0.07\times10^8$ W Ω K^{-3} for the group(11) metals at 0 °C[11]). Hence we expect a decrease in c for gold due to relativistic effects (in J cm^{-1} s^{-1} K^{-1} at 0 °C): Cu 3.85, Ag 4.18, Au 3.1.[11] Also the electronic heat capacity γ for gold shows an unexpected behavior (in 10^{-4} J K^{-1} mol^{-1} below 4 K): Cu 6.926, Ag 6.411, Au 6.918.[42] Indeed Kupratakuln and Fletcher found a nonrelativistic value which is smaller by about 6%, using the augmented plane wave method (APW) for their band structure calculations.[38] Further investigation of this area would be extremely interesting.

From Pauling's treatment of bond energies in free molecules[43] we see that the dissociation energy is dependent upon the relativistic change in the electronegativity of the ligand. This formula correctly describes the relativistic behavior qualitatively but yields quantitatively poor results.[44] Nevertheless, this treatment has been adopted by Eley[45] and extended by Flores *et al.*[46] for estimating adsorption energies of chemisorbed states:

$$E(\text{M–A}) = m(\text{EN}_\text{M}-\text{EN}_\text{A})^2 + n[E(\text{M–M}) + E(\text{X–X})] + f_s \quad (3)$$

Here E(M–M) and E(X–X) are the single bond energies of the metal and the diatomic molecule, EN the corresponding electronegativities, n, m, and f_s are structural factors.[47] With this formula Flores *et al.* calculated energies of chemisorption for different molecules on various surfaces. The values of the energy of chemisorption for the group(11) series obtained are of special interest here[47] (in eV): Cu/N_2 4.2, Ag/N_2 5.0, Au/N_2 2.5; Cu/O_2 5.4, Ag/O_2 6.0, Au/O_2, 3.6; Cu/NO 9.6, Ag/NO 11.0, Au/NO 6.1; Cu/H_2 2.4, Ag/H_2 2.5, Au/H_2 2.5. The values calculated are normally in good agreement with experimental data.[48] The destabilization for molecules containing electronegative atoms is evident whereas for H_2 the same chemisorption energy is obtained for Au and Ag surfaces. These values are dependent on relativistic effects in the difference of the metal–ligand electrone-

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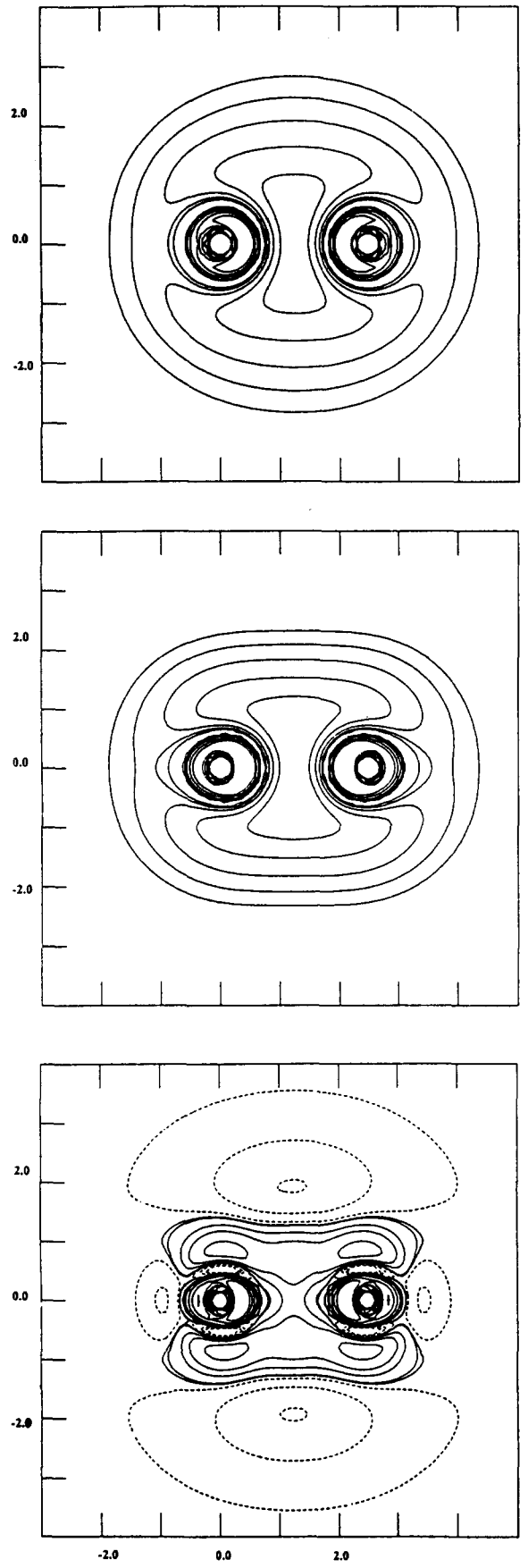

FIG. 10. Contours of electron density of the HOMO of Au_2 calculated from HF wave functions (a) nonrelativistic density ρ^{NR} (b) relativistic ρ^{R} (c) difference density $\Delta_R\rho = \rho^{NR} - \rho^{R}$. The full lines show the negative part and the dashed line the positive part of $\Delta_R\rho$. The gold atoms are situated at 0.0 and 2.472 Å on the horizontal axis and 0.0 on the vertical axis.

gativities as well as on the relativistic change in E(M–M) if we neglect relativistic effects in E(X–X). The first factor is quite sensitive to the nature of the ligand because of the square in $(EN_M - EN_X)$, whereas the second term in Eq. (3) leads only to a relativistic correction dependent on the nature of the surface. From our calculated relativistic correction to the dissociation energy (destabilizations for electronegative and stabilizations for electropositive ligands) or from $\Delta_R EN = -0.4$ we see immediately that the special behavior of the Au surfaces is a relativistic effect.

Concerning cluster molecules, a large number of these are known for gold,[49] but only a few copper clusters have been found[50] and silver clusters are very rare.[51] Indeed, a significant increase in bond stability was found in gold clusters which is probably due to relativistic effects (in kJ/mol): Cu_3 294 ± 13, Ag_3 253 ± 13, Au_3 367 ± 13.[52] Also, intermolecular Au–Au interactions are well known in inorganic and organometallic chemistry,[53] while this is not the case for silver and copper compounds.

The effect of the relativistic Au 6*s* orbital contraction can be examined in the electron density plots calculated from both nonrelativistic and relativistic calculations (HF) for the Au_2 molecule at the experimental bond length, Figs. 10 (a) and 10 (b). A higher density of contours closer to the nucleus can be clearly seen for the relativistic calculation, Fig. 10 (b). The difference density shows regions of increased relativistic density in the bond region which agrees well with the calculated relativistic increase in the dissociation energy. In the outer region along the internuclear axis the negative areas correspond to the relativistic expansion of the d_σ components of the HOMO, Fig. 10 (c).

2. $Au^{-\delta}$ compounds

The most electropositive ligands are the alkali metals. No stable intermetallic compounds of copper and silver are known, except $NaAg_2$.[54] The diatomic alkali metal copper and silver species have only detected by mass spectroscopic methods.[14] In contrast to this, gold forms intermetallic compounds with all alkali metals. RbAu and CsAu are ionic, semiconductors, and crystallize with CsCl structure.[55] The ionic character of these compounds has been pointed out earlier,[56] and the nonrelativistic species would be metallic alloys as we would normally expect.[57] The other gold–alkali compounds (X = Li,Na,K) are metallic in nature and structural data for the solid state are not available (LiAu has not been observed in stoichiometric composition[56]). Nevertheless, the phase diagrams of the gold–alkali compounds all show stable phases close to the 1:1 stoichiometry.[55] This is not the case for the silver or copper compounds.[54] From mass spectrometric measurements only the dissociation energies for some group(11) alkali compounds are known[14] (in kJ/mol): CuLi 191, AgLi 175, AuLi 281; CuNa 173, AgNa 135, AuNa 210. Obviously, the relativistic effects are the reason for the increased stability of the gold-alkali compounds (see Table II). The still unknown cohesive energies of the corresponding solids are expected to show the same trend in stability as the diatomics. Only AuCs has been studied previously by Ziegler and co-workers using a quasirelati-

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vistic Hartree–Fock–Slater method,[58] but this method often overestimates relativistic effects.

3. $Au^{+\delta}$ compounds

In Fig. 5 we have shown the reduced bond stability of the gold halides, which is due to the reduced ionicity of the bond. We, therefore, expect smaller intermolecular electrostatic interactions (because of reduced dipole moment). Indeed, the structures of the gold halogenides differ completely from the silver and copper compounds.[4] The gold fluorides have been reviewed recently by Müller.[10] AuF has not yet been isolated and thermodynamic data suggest that it would disproportionate to Au and AuF_3.[4] Also AuF_2^- is not known; not even mixed $AuFX^-$ complexes (X = Cl,CN,...) have been reported yet. All other diatomic Au(I) halogenides have been reported to be (more or less) stable.[4] The large relativistic bond destabilization in AuF (75 kJ/mol, Table I) is probably one reason, and one may also speculate that relativity stabilizes the $5d$ bonding of Au^{3+}, but calculations on AuF_3 are necessary to decide further. It would also be interesting to perform accurate CI calculations at both the nonrelativistic and relativistic level, to get more appropriate results for $\Delta_R D_e$. Nevertheless, AuF is stable with respect to its dissociation products and it should be possible to observe it by gas phase or matrix isolation spectroscopic methods.

F. Correlation effects

The calculated CI results are given in Tables I, III, and IV. The zero point vibrational frequency correction to the dissociation energy has been neglected due to the large experimental inaccuracy. For the few experimentally measured closed shell cases our CI results agree very well with experiment. In fact, for AuH, AuLi, and AuNa we nearly reproduce the experimental dissociation energy at the CEPA-1 level. We, therefore, performed nonrelativistic CI calculations for AuH, AuLi, and AuF using the same quality of basis sets as described in Sec. III. The relativistic changes at the CISD (CISD/SC) level for AuH are: $\Delta_R r_e = 0.286(0.294)$ Å, $\Delta_R D_e = -139.1(-151.5)$ kJ/mol, $\Delta_R k_e = -1.711(-1.770)$ mdyn/Å; for AuLi: $\Delta_R r_e = 0.258(0.251)$, $\Delta_R D_e = -174.1(-178.5)$, $\Delta_R k_e = -0.334(-0.347)$; for AuF: $\Delta_R r_e = 0.180(0.182)$, $\Delta_R D_e = +86.0(+79.2)$, $\Delta_R k_e = -0.724(-0.719)$. Hence, the relativistic effects are even larger at the CI compared to the HF level. This is understandable in the case of the dissociation energy since the $6s$ electron is relativistically more localized at the Au atom than in the nonrelativistic case and this leads to larger correlation contributions at the relativistic level. Nevertheless, our calculated relativistic effects at the HF level are quite reasonable for predicting the trends in relativistic changes of molecular properties and we expect the same behavior at the CI level. For example, if we compare our calculated CI force constants with the measured values for the copper and silver halogenides[33] we see exactly the same trend in the group(11) series as shown in Fig. 9., e.g., a relativistic increase in the Au–X force constant.

The calculated CI dissociation energies of the open-shell cases AuO and AuS do not agree satisfactorily with experiment. Even at the CEPA-1 level we obtain only about 60% of the correlation energy for AuO and AuS. It is well known that open-shell systems are more difficult to treat because they show larger amounts of single and triple substitutions in the CI wave function compared to closed shell cases. To achieve better results, an extension of the basis set and a full CI treatment would be necessary. Also, size-consistency effects are most important. For example, in Au_2 the CISD procedure yields only a very small increase in the dissociation energy of about 14 kJ/mol, whereas the Davidson corrected CI and the CEPA-1 procedure yield 71 and 112 kJ/mol, respectively. The total amount of the correlation energy is about 156 kJ/mol. Recently, Balasubramanian published CI calculations on Au_2 and Au_3.[59] He obtained about 95 kJ/mol correlation energy for Au_2 using a multireference CISD. Also, his calculated CI dissociation energy for Au_3 with 193 kJ/mol is small compared to the experimental level (367 kJ/mol[52]). This clearly shows the need of size-consistent multireference CI procedures including higher excitations to get more reasonable results. However, such methods are very time and disk-space consuming, especially if excitations from the $5d$ core are allowed.

The reported AuCl dissociation energy of about 340 kJ/mol[60] is significantly larger than the calculated one and needs remeasurement, since such a discrepancy does not show up for the other members of this series (e.g., compare with the more accurate experimental dissociation energy of

TABLE V. Pseudopotential parameters for Au, Br, and I [Eq. (4)].

	Au (NRPP)		Au (ARPP)		Br (ARPP)		I (ARPP)	
1	B_{1k}	b_{1k}	B_{1k}	b_{1k}	B_{1k}	b_{1k}	B_{1k}	b_{1k}
0	432.047 072	12.532 20	426.709 840	13.205 10	61.513 721	5.0218	83.113 863	3.5112
0	81.627 162	6.594 55	35.938 824	6.602 55	9.021 493	2.5109	5.201 876	1.7556
1	263.062 122	10.706 33	261.161 023	10.452 02	53.875 864	4.2814	82.811 109	2.9688
1	43.725 251	5.223 73	26.626 284	5.226 01	4.629 402	2.1407	3.379 682	1.4844
2	124.243 091	7.841 47	124.756 831	7.851 10	20.849 677	2.8800	10.304 277	1.9066
2	17.676 351	3.925 89	15.772 260	3.925 55	2.965 444	1.4400	7.588 032	0.9533
3	22.011 203	4.728 50	30.568 475	4.789 80	− 8.161 493	2.7207	− 21.477 936	2.3075
3	9.849 459	3.007 01	5.183 774	2.394 91				

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TABLE VI. Basis sets for Au, Br, and I. In the case of the negative charged molecules (Au_2^- and AuH^-) as well as for AuLi and AuNa two additional diffuse functions with the exponents 0.003 and 0.001 for ARPP and one with exponent 0.001 for NRPP have been used. α_i: exponent; c_i: contraction coefficient.

	α_i	c_i	α_i	c_i	α_i	c_i
Au NRPP	16.441 608	0.147 289	10.326 333	0.083 165	5.584 479	− 0.060 360
	11.441 608	− 0.470 147	5.615 305	− 0.330 755	1.696 575	0.376 402
	4.605 939	1.0	1.616 456	0.548 486	0.676 002	1.0
	1.337 144	1.0	0.740 360	0.546 721	0.235 117	1.0
	0.591 519	1.0	0.285 886	1.0	0.074 066	1.0
	0.154 073	1.0	0.063 903	1.0		
	0.050 970	1.0				
	0.014 035	1.0				
	0.004 535	1.0				
Au ARPP	30.196 537	0.004 733	13.838 219	0.036 179	6.337 001	− 0.044 103
	9.725 973	− 0.354 382	5.195 787	− 0.328 303	1.480 697	0.462 115
	5.080 406	1.0	1.798 045	0.665 388	0.528 382	1.0
	1.722 657	1.0	0.666 105	0.552 666	0.171 117	1.0
	0.726 459	1.0	0.154 336	1.0	0.045 512	1.0
	0.090 354	1.0	0.034	1.0		
	0.022 106	1.0				
	0.006 415	1.0				
Br ARPP	150.601 735	0.0 014 570	41.713 235	0.000 188	0.389	1.0
	4.829 122	0.0 412 462	5.260 912	0.070 723		
	2.210 371	1.0	2.714 091	1.0		
	0.507 162	1.0	0.594 472	1.0		
	0.326 043	1.0	0.230 393	1.0		
	0.120 275	1.0	0.072 212	1.0		
	0.045	1.0				
I ARPP	10.741 271	0.0 299 120	8.651 963	0.005 258	0.266	1.0
	7.685 960	− 0.116 339	2.850 229	− 0.313 149		
	3.842 560	1.0	1.867 716	1.0		
	1.526 500	1.0	0.376 669	1.0		
	0.285 520	1.0	0.154 766	1.0		
	0.102 544	1.0	0.052 839	1.0		
	0.040	1.0				

379 kJ/mol for CuCl and 311 kJ/mol for AgCl[14]). Dipole moments for gold compounds are unknown, therefore, we can give no analysis of the accuracy of our calculated CEPA-1 values as listed in Table IV.

III. CALCULATIONAL DETAILS

Our procedure has been described in detail in previous papers.[61] Relativistic effects are included by adjusting the pseudopotential parameters to spin–orbit averaged Dirac–

TABLE VII. Total energies (a.u.) for the atoms used in the molecular calculations. HF: from numerical HF calculations using program MCHF (Ref. 19). AA: algebraic approximations using the basis sets of Table II for pseudopotentials and the basis sets given in Csizmadias book (Ref. 63). The ARPP/HF results are derived from Dirac–Fock (DF) calculations using program MCDF/BENA (Ref. 20). The index is given in Ref. 63.

	Index	Contraction	HF	AA
H	1.4.1	(1111111/11)	5.000 000 0 − 1	4.999 486 4 − 1
Li	3.28.2	(6211111/1111)	7.432 726 9 + 0	7.432 706 5 + 0
O	8.76.2	(6211111/4211/1)	7.480 939 8 + 1	7.481 098 2 + 1
F	9.71.2	(6211111/4211/1)	9.940 934 9 + 1	9.940 989 3 + 1
Na	11.15.2	(631111/42111/1)	1.618 589 1 + 2	1.618 460 2 + 2
S	16.25.1	(631111/52111/1)	3.975 049 0 + 2	3.974 978 6 + 2
Cl	17.21.1	(6311111/521111/1)	4.594 820 7 + 2	4.594 737 9 + 2
Cu	Ref.15(f)	(85411111/331111/3111)	1.638 963 7 + 3	1.638 787 3 + 3
Br	35.7.1	(63111111/333111/411)	2.572 441 3 + 3	2.572 343 9 + 3
Br	ARPP	(211111/21111/1)	1.312 391 0 + 1	1.312 055 3 + 1
Ag	Ref.64	(432111111/42211/3111)	5.197 517 9 + 3	5.192 272 9 + 3
I	53.3.1	(4321111/421111/4111)	6.917 980 9 + 3	6.912 714 4 + 3
I	ARPP	(211111/21111/1)	1.117 804 4 + 1	1.117 807 3 + 1
Au	ARPP	(2111111/411/2111)	1.349 293 6 + 2	1.349 327 3 + 2
Au^-	ARPP	(211111111/411/2111)	1.349 537 9 + 2	1.349 566 4 + 2
Au	NRPP	(21111111/411/2111)	1.308 356 6 + 2	1.308 273 3 + 2
Au^-	NRPP	(211111111/411/2111)	1.308 393 0 + 2	1.308 312 0 + 2

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TABLE VIII. Ionization energies and electron affinities for Au, Br, and I in eV. The experimental Au^+ $^2F(5d^86s^1)$ value is approximated from the atomic energy levels of Pt. The DF Au ($5d^{10}6d^1$) value is approximated from HF values and relativistic effects from the $5d^{10}6d^1$ spectra of Tl^{2+} and Pb^{3+}. Experimental values from Refs. 18 and 71 are spin–orbit averaged.

Au→	Au^- $6s^2$	Au $6p^1$	Au $6d^1$	Au $5d^96s^2$	Au^+	Au^+ $5d^96s^1$	Au^{2+} $5d^9$	Au^{3+} $5d^8(^3F)$
HF	−0.0990	2.7117	4.4389	5.1311	5.9159	11.695	26.025	58.194
NRPP	−0.1033	2.7207	4.4511	5.1497	5.9280	11.719	26.060	58.181
DF	−0.6648	4.2335	6.1944	1.8855	7.6744	9.950	26.833	57.777
ARPP	−0.6481	4.2647	6.1891	1.9273	7.6613	9.966	26.868	57.857
exp.	−2.3086	4.9473	7.6872	1.7446	9.2257	11.513	29.7	···
MP2	−2.1229	···	···	···	9.0756	11.941	29.783	62.140
CISD	−1.5642	···	···	···	8.6352	11.344	28.862	60.903
CISD/SC	−1.9134	···	···	···	8.8494	11.572	29.228	61.382
Br,I→	Br^-	Br^+	Br^{2+}	Br^{3+}	I^-	I^+	I^{2+}	I^{3+}
DF	−2.5225	10.686	30.380	65.412	−2.4972	9.417	26.354	56.833
ARPP	−2.5483	10.732	30.721	65.544	−2.5089	9.556	26.975	56.976
exp.	−3.518	11.877	33.283	···	−3.374	10.525	29.243	···
CISD	−3.166	11.465	32.400	67.572	−2.995	10.209	28.540	58.870
CISD/SC	−3.271	11.538	32.528	67.723	−3.087	10.281	28.669	59.023

Fock energies (ARPP).[61] To avoid intercore penetration and core polarization effects,[23,34,62] we have chosen a 19 valence electron [$Kr4f^{14}$] core pseudopotential. A multielectron fit procedure has been carried out using the following functional form of the pseudopotential[61]:

$$V_P^\lambda = \sum_{\substack{l\in\text{core} \\ \lambda\in\text{atoms}}} P_{l\lambda} \sum_{k=1,2} B_{l\lambda k} \exp(-b_{l\lambda k} r_\lambda^2) . \qquad (4)$$

Such a procedure has the advantage that it avoids large changes in the core by electron occupancy of the noncore orbitals.[23] We took also care in our fit procedure that the pseudovalence orbitals represent the correct shape and size of the HF orbitals in regions outside the defined [$Xe4f^{14}$] core. Since relativistic effects may also be important in Br and I compounds,[61] we also performed calculations on AuBr and AuI using ARPPs for bromine and iodine. The pseudopotential parameters for Au, Br, and I are presented in Table V. The basis sets used for the ARPPs are shown in Table VI. The derivation of the basis sets has already been described.[25] The basis sets used for the ligands are summarized in Table VII. The additional diffuse and polarization functions are taken from Ref. 63 if available, otherwise from Ref. 64. The first ionization potentials and the electron affinities for the atoms are given in Table VIII, compared to results obtained from numerical HF and DF calculations (HF limit).[19,20] Table VIII shows that the multielectron energy-adjusted pseudopotentials represent excellently the corresponding HF and DF values (with errors less than 2.5%), and hence should be accurate enough for our molecular calculations. We wish to point out that in the case of Au the relativistic effects on the ionization energies exceed the correlation effects. Therefore, results comparable to experiment can be only achieved by including relativistic effects.

The SCF calculations have been performed using Davidson's program MELD[65] and an extended version of GAUSSIAN 86 for pseudopotentials.[66] The CISD and CEPA-1[67] calculations have been carried out using Meyer's program MOLPRO[68] and GAUSSIAN 86.[66] The size consistency correction is that of Langhoff and Davidson.[69] The basis sets used for the CI and CEPA calculations are the same as described in Tables VI and VII, but extended by an f function of Au with exponent 1.1447. The active CI space has been limited to reduce the size of the CI configurations (which has been between 40 000 and 200 000 depending on the gold species calculated). For example, the ($5s5p$) space for Au has been kept inactive for all compounds. For the atomic CI calculations the basis sets in Table VI has been extended by an additional ($2s/2p/2d/3f$) function set for Au and a ($3s/2p/2d/2f$) set for Br and I. The active CISD space is complete within this basis set. Considering the limited basis set used and the inclusion of only up to double substitutions in the CI wave function, the atomic CI results for Au, Br, and I are in good agreement with experiment. We also listed MP2 (second-order Møller–Plesset[70]) results for Au because it has often been suggested, that this treatment of correlation yields poor results for the transition metals. As we see from Table VI, the MP2 results for gold give very good agreement with experiment.

IV. SUMMARY

In this article the important role of relativistic effects in gold chemistry has been demonstrated. The relativistic "Au maximum" pointed out by Pyykkö and Desclaux[9] has a large effect on the properties of gold and its compounds. The relativistic bond contractions are large (between 0.16 and 0.42 Å), often resulting in the AuX bond lengths being smaller than those of the corresponding silver species. AuH^+ is a special case, because of its low stability at the nonrelativistic level (the opposite situation occurs for TlH^+,

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which is unstable at the relativistic level[25]). It is clear that the relativistic change in the bond stabilities influences the solid state properties. In many cases, gold compounds have structures completely different from the corresponding silver and copper compounds. The relativistic bond stabilization is dependent on the ligand electronegativity, showing the largest stabilization for the alkali–metals and the largest destabilizations for the halogens. In group(11) only gold forms stoichiometric compounds with all alkali metals. On the other hand, AuF has not been detected yet, whereas gas phase CuF and AgF are well known. The force constants increase in all cases, even when there are large energetic bond destabilizations as is the case for AuF. The vibrational frequencies are therefore shifted to higher values, in some cases by more than 50%. The ionicity is decreased in gold compounds with electronegative ligands, showing a decrease in the dipole moment of 2–3 D. The possible implications for the structure of gold compounds have been discussed.

We have presented a large number of as yet unmeasured spectroscopic constants. The pseudopotentials used are accurate enough to produce results of all-electron HF or DF quality. However, spin–orbit interactions have been neglected, because they are expected to be small for compounds of gold with closed $5d$ shell and open $6s$ shell. Where measured data are available, our values agree in most cases very well with experiment. A large amount of chemistry of Au(I) has been rationalized with the help of the ionic model in which AuF and AuLi are considered as two limiting extremes. Concerning Au(III), one has to consider the open $5d$ shell and covalent contributions may become more important. Relativistic effects reduce the $5d/6s$ separation and enlarge the $6s/6p$ separation significantly (Fig. 2). Since the $5d$ shell is fully occupied and the $6p$ shell is empty in the free atom, we expect an increase in $5d$ and a decrease in $6p$ involvement in AuX bonds due to relativity. Gold $6p$ orbitals are found to be unimportant in diatomic Au(I) compounds at the HF level. In general, the HOMOs are composed of Au $5d$ and $6s$ AOs, while the LUMOs have large $6p$ admixture. CI calculations show an increased mixing of the $6p$ into the ground states. The scattered wave $X\alpha$ approximation yields larger p populations for similar compounds already at the SCF level.[72] However, the $6p$ involvement in the Au–X bond may become more important in polynuclear Au(I) or Au(III) compounds such as AuX_2^- or AuX_4^-. Nonrelativistic and relativistic calculations on such species would be interesting. Due to electron withdrawal, electronegative ligands support more $5d$ contribution, whilst electropositive ones do not. Hence we expect the stability series $AuX < AuX_2^- < AuX_4^-$ for electronegative ligands which should be reversed for the more electropositive ligands since such compounds need $6p$ involvement. This may explain the preference of higher oxidation states for the gold halogenides in contrast to the organo–gold compounds. Similarly, Pyykkö argues in his review article,[2] that Au(III) compounds containing electronegative ligands should be relativistically stabilized because of the relativistic destabilization of the atomic $5d$ level in Au (Table VIII). Zwanziger *et al.* found for such compounds an electron transfer to the ligand of less than one electron.[73] The different stabilities of organic and inorganic gold compounds, mentioned at the beginning of Sec. I, is a still unsolved but interesting problem and needs more theoretical investigation. A detailed analysis will be published in near future.

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[1] A complete reference list of studies in relativistic effects in Au compounds is given in the recently published review article of P. Pyykkö (see Ref. 2).
[2] P. Pyykkö, Chem. Rev. **88**, 563 (1988).
[3] W. H. E. Schwarz, in *Theoretical Models of Chemical Bonding* (Springer, Heidelberg, 1989), Vol. 2.
[4] (a) R. J. Puddephat, *The Chemistry of Gold* (Elsevier, Amsterdam, 1978); (b) R. J. Puddephat, in *Comprehensive Coordination Chemistry*, (Pergamon, Oxford, 1987), Vol. 5.
[5] H. Gilman, L. A. Woods, J. Am. Chem. Soc. **70**, 550 (1948).
[6] E. W. Abel and F. G. A. Stone, *Organometallic Chemistry* (The Royal Society of Chemistry, London, 1971–1987), Vols. I–XV.
[7] (a) P. Schwerdtfeger, P. D. W. Boyd, G. A. Bowmaker, H. G. Mack, and H. Oberhammer, J. Am. Chem. Soc. **111**, 15 (1989); (b) P. Schwerdtfeger, H. Silberbach, and B. Miehlich, J. Chem. Phys. **90**, 762 (1989).
[8] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, Oxford, 1984).
[9] (a) P. Pyykkö and J. P. Desclaux, Nature **266**, 337 (1977); (b) K. S. Pitzer, Acc. Chem. Res., **12**, 271 (1979); (c) P. Pyykkö and J. P. Desclaux, Acc. Chem. Res. **12**, 276 (1979); (d) P. Pyykkö, Adv. Quantum Chem. **11**, 353 (1978); (e) J. P. Desclaux, and P. Pyykkö, Chem. Phys. Lett. **39**, 300 (1976).
[10] (a) B. G. Müller, Angew. Chem. Int. Ed. Engl. **26**, 1081 (1987); (b) A. A. Timakov, V. N. Prusakov and Y. V. Drobysheskii, Dokl. Akad. Nauk SSSR. **291**, 125 (1986).
[11] (a) R. C. Weast, M. J. Astle, and W. H. Beyer, *Handbook of Chemical Physics*, 68th ed. (Chemical Rubber, Boca Raton, Florida, 1988); (b) T. Matsubara, *The Structure of Properties of Matter* (Springer, Heidelberg, 1982), p. 21.
[12] According to the BCS theory the superconducting transition temperature is proportional to the electronic density of states at the Fermi surface, which is dependent on relativistic effects in the $6s$ and $5d$ bands (at a fixed geometry), and on the relativistically caused change in the solid state structure. It seems likely that the nonrelativistic T_c for Hg would be less than 0.5 K. For gold compounds with superconducting properties, see, for example, N. Jisrawi, W. L. Mclean and N. G. Stoffel in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 29.
[13] (a) S. J. Rose, I. P. Grant, and N. C. Pyper, J. Phys. B **11**, 1171 (1978); (b) W. H. E. Schwarz, E. van Wezenbeck, E. J. Baerends, and J. Snijders, J. Phys. B (submitted); (c) E. J. Baerends, P. Schwerdtfeger, and W. H. E. Schwarz (to be published).

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[14](a) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules* (Van Nostrand, New York, 1979); (b) A. Neubert and K. F. Zmbov, J. Chem. Soc. Faraday Trans. 1, **70**, 2219 (1974); (c) V. Piacente and K. A. Gingerich, High Temp. Sci. **9**, 189 (1977); (d) H. R. Ihle, E. Langenscheidt, and B. Zmbova, J. Chem. Phys. **66**, 5105 (1977); (e) J. S. Gole, in *Metal Clusters*, edited by M. Moskovits (Wiley, New York, 1986).

[15](a) H. Stoll, P. Fuentealba, J. Flad, L. v. Szentpály, and H. Preuss, J. Chem. Phys. **79**, 5532 (1983); (b) H. Stoll, P. Fuentealba, P. Schwerdtfeger, J. Flad, L. v. Szentpály, and H. Preuss, J. Chem. Phys. **81**, 2732 (1984); (c) S. Huzinaga, M. Klobukowski, Z. Barandiaran, and L. Seijo, J. Chem. Phys. **84**, 6315 (1986); (d) M. T. Nguyen, M. A. McGinn, and N. J. Fitzpatrick, J. Chem. Soc. Faraday Trans. 2 **82**, 1427 (1986); (e) *International Tables for X-Ray Crystallography, The International Union of Crystallography* (Kynoch, Birmingham, 1962); (f) P. Schwerdtfeger, L. P. Aldridge, G. A. Bowmaker, and P. D. W. Boyd, J. Chem. Phys. (submitted); (g) R. L. Martin, J. Chem. Phys. **86**, 5027 (1987); (h) C. W. Bauschlicher, S. R. Langhoff, H. Partridge, and S. P. Walch, *ibid.* **86**, 5603 (1987).

[16]N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University, Ithaca, New York, 1933).

[17]R. S. Nyholm, Proc. Chem. Soc. London **1961**, 273.

[18]C. E. Moore, *Atomic Energy Levels* (U.S.GPO, Washington, D.C., 1958).

[19]C. Froese-Fischer, Comp. Phys. Commun. **14**, 145 (1978), modified for pseudopotentials by M.Dolg (1987).

[20]I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comp. Phys. Commun. **21**, 207 (1980).

[21]T. Itoh, Rev. Mod. Phys. **37**, 159 (1965).

[22](a) J. N. Bardsley, Case Stud. At. Phys. **4**, 299 (1974); (b) R. N. Dixon and I. L. Robertson, Spec. Per. Rep. Theo. Chem. **3**, 100 (1978); (c) J. C. Barthelat and Ph. Durand, Gazz. Chim. Ital. **108**, 225 (1978); (d) M. Krauss and W. J. Stevens, Annu. Rev. Phys. Chem. **35**, 357 (1984); (e) P. A. Christiansen and K. S. Pitzer, Annu. Rev. Phys. Chem. **36**, 407 (1985).

[23]U. Wedig, Thesis, Stuttgart, 1988.

[24]The forthcoming papers will deal relativistic calculations on Au(III), organogold and gold cluster compounds.

[25]P. Schwerdtfeger, Phys. Scr. **36**, 453 (1987).

[26]W. H. E. Schwarz, Phys. Scr. **36**, 403 (1987).

[27]J. G. Snijders and P. Pyykkö, Chem. Phys. Lett. **75**, 5 (1980).

[28]*Periodic Table of the Elements* (E. H. Sargent, Cincinnati, 1966).

[29]P. J. Hay, W. Wadt, L. R. Kahn, and F. W. Bubrowitz, J. Chem. Phys. **69**, 984 (1978).

[30]H. Basch and S. Topiol, J. Chem. Phys. **71**, 802 (1979).

[31]D. L. Lichtenberger and R. F. Fenske, Program MOPLOT, Quantum Chemistry Program Exchange, Program No. 284.

[32](a) J. C. A. Boeyers and R. H. Lemmer, J. Chem. Soc. Faraday Trans. 2 **73**, 321 (1977); (b) W. J. Pietro and W. J. Hehre, J. Comput. Chem. **4**, 241 (1983); (c) H. Beckmann, G. Pacchioni, and G. H. Jeung, Chem. Phys. Lett. **116**, 423 (1985); (d) C. W. Bauschlicher, S. R. Langhoff, and H. Partridge, J. Chem. Phys. **87**, 5603 (1987).

[33]G. A. Bowmaker, in Adv. Spectrosc. **14**, 1 (1987).

[34]P. Schwerdtfeger, Thesis, Stuttgart, 1987.

[35]J. Overend, in *Infrared Spectroscopy and Molecular Structure*, edited by M. M. Davies (Elsevier, Amsterdam, 1963).

[36]It should be realized that the existence of the fundamental physical constant c is a consequence only of the principle of relativity (axiom of the special relativity; see Ref. 37). Rigorously, the laws of classical mechanics are obtained by $c \to \infty$ where spectroscopic intensities would approach zero.

[37]R. U. Sexl and H. K. Urbantke, *Relativität, Gruppen, Teilchen* (Springer, Heidelberg, 1976); pp. 6–8.

[38](a) S. Kupratakuln and G. C. Fletcher, J. Phys. C **2**, 1886 (1969); (b) S. Kupratakuln, *ibid.* **3**, S109 (1970); (c) N. E. Christensen and S. O. Seraphin, Solid State Commun. **44**, 57 (1982); (d) J. Keller and A. Pisanty, M. del Carmen de Teresa, and M. Erbudak, Phys. Lett. A **71**, 90 (1979); (e) T. Takeda, J. Phys. F **10**, 1135 (1980); (f) O. Jepsen, D. Glötzel, and A. R. Mackintosh, Phys. Rev. B **23**, 2684 (1981).

[39]N. E. Christensen, Int. J. Quantum Chem. **25**, 233 (1984).

[40]N. E. Christensen, Phys. Rev. B **4**, 3321 (1971).

[41](a) J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974); A. V. Zhalko-Titarenko, V. N. Antonov, V. V. Nemoshkalenko, and W. John, Phys. Status Solidi B **132**, K15 (1985).

[42]D. L. Martin, Phys. Rev. **170**, 650 (1968).

[43]L. Pauling, *The Nature of the Chemical Bond* (Cornell University, Ithaca, 1960).

[44]P. Schwerdtfeger (unpublished results).

[45]D. D. Eley, Discuss. Faraday Soc. **8**, 34 (1950).

[46]F. Flores, I. Gabbay, and N. H. March, Chem. Phys. **63**, 391 (1981).

[47]N. H. March, *Chemical Bonds Outside Metal Surfaces* (Plenum, New York, 1986).

[48]T. N. Rhodin and G. Ertl, *The Nature of the Surface Chemical Bond* (North-Holland, Amsterdam, 1979).

[49](a) K. P. Hall and D. M. P. Mingos, Prog. Inorg. Chem. **32**, 237 (1984); (b) D. M. P. Mingos and R. L. Johnston, in *Structure Bonding 68* (Springer, Berlin, 1987).

[50]G. VanKoten and J. G. Noltes, in *Comprehensive Organometallic Chemistry*, edited by G. Wilkinson, F. G. A. Stone, and E. W. Abel (Pergamon, Oxford, 1982), Vol. 2, p. 709.

[51]C. E. Briant, R. G. Smith, and D. M. P. Mingos, J. Chem. Soc. Chem. Commun. **1984**, 586.

[52](a) K. Hilpert and K. A. Gingerich, Ber. Bunsenges. Phys. Chem. **84**, 739 (1980); (b) J. L. Gole, in *Metal Clusters*, edited by M. Moskovits (Wiley, New York, 1986).

[53](a) P. G. Jones, Gold Bull. **16**, 114 (1983); (b) H. Schmidbaur, W. Graf, and G. Müller, Angew. Chem. Int. Ed. Engl. **27**, 417 (1988).

[54]B. W. Mott, *Compounds and Alloys of the Alkali Metals*, Special Publication 22 (The Chemical Society, London, 1967).

[55]G. Kienast and J. Verma, Z. Anorg. Allg. Chem. **310**, 143 (1961).

[56](a) W. J. Peer and J. J. Lagowski, J. Am. Chem. Soc. **100**, 6260 (1978); (b) N. E. Christensen, Phys. Rev. B **32**, 207 (1985).

[57]N. E. Christensen and J. Kollar, Phys. Rev. B **29**, 6481 (1984).

[58](a) T. Ziegler, J. G. Snijders, and E. J. Baerends, Chem. Phys. Lett. **75**, 1 (1980); (b) J. Chem. Phys. **74**, 1271 (1981).

[59]K. Balasubramanian and M. Z. Liao, J. Chem. Phys. **86**, 5587 (1987).

[60]W. F. C. Ferguson, Phys. Rev. **31**, 969 (1928).

[61](a) P. Schwerdtfeger, L. v. Szentpály. K. Vogel, H. Silberbach, H. Stoll, and H. Preuss, J. Chem. Phys. **84**, 1606 (1986); (b) M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *ibid.* **86**, 866 (1987).

[62]U. Wedig, M. Dolg, H. Stoll, and H. Preuss, in *Quantum Chemistry; The Challenge of Transition Metals and Coordination Chemistry*, edited by A. Veillard (Reidel, Dordrecht, 1986), p. 79.

[63]R. Poirier, R. Kari and I. G. Csizmadia, *Handbook of Gaussian Basis Sets, Physical Sciences Data 24* (Elsevier, Amsterdam, 1985).

[64]S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).

[65]L. McMurchie, S. Elbert, S. Langhoff, and E. R. Davidson, program MELD, Washington University, Seattle; 1982.

[66]M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, program GAUSSIAN 86, Carnegie–Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA, 1984, extended for local and nonlocal pseudopotentials by P. Schwerdtfeger using program PSEPOT for the latter: M. Kolar, Comp. Phys. Commun. **23**, 275 (1981).

[67](a) W. Meyer, J. Chem. Phys. **58**, 1017 (1973); (b) **64**, 2901 (1976); (c) W. Kutzelnigg, in *Methods in Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977).

[68]W. Meyer and H. J. Werner, program MOLPRO, Universität Kaiserslautem and Frankfurt 1987.

[69]S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).

[70]C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[71](a) Landoldt-Börnstein, *Atom und Molekularphysik* (Springer, Heidelberg, 1950); (b) H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).

[72]G. A. Bowmaker, P. D. W. Boyd, and R. J. Sorrenson, J. Chem. Soc. Dalton Trans. **81**, 1627 (1985).

[73](a) J. Reinhold, H. Zwanziger, E. Hoyer, and C. Zwanziger, Z. Chem. **14**, 314 (1974); (b) H. Zwanziger, J. Reinhold, and E. Hoyer, *ibid.* **15**, 69 (1974).

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