

Table IX  
Molecular Constants for AuH

$R_e$ , calcd nonrel, Å	1.807, <sup>a</sup> 1.747 <sup>b</sup>
calcd relativ, Å	1.522, <sup>a</sup> 1.622 <sup>b</sup>
exptl, Å	1.524 <sup>c</sup>
$D_e$ , calcd relativ, eV	2.66 <sup>a</sup>
exptl, eV	3.37 <sup>c</sup>

<sup>a</sup> Effective potential method.<sup>24</sup> <sup>b</sup> One-center method.<sup>27</sup>  
<sup>c</sup> Experimental.<sup>28</sup>

culations can be made relativistically as well as non-relativistically, and the difference may give a useful measure of the relativistic effect even where the absolute value of the calculated property is not very accurate. Other approximate calculations including relativistic features are reviewed by Pyykkö.<sup>3</sup>

It is interesting to compare the relativistic effects in AuH with those in Au<sub>2</sub>. There are effective potential calculations of Hay et al.<sup>24</sup> and one-center calculations of Desclaux and Pyykkö<sup>27</sup> which are given in Table IX together with experimental values.<sup>28</sup> The effective potential method yields excellent agreement with experiment for the bond distance, with a relativistic shortening of 0.28 Å as compared to 0.35 Å in Au<sub>2</sub>.

### Direct Consequences of Spin-Orbit Energies

In addition to the effects on bond energies, there are other consequences when spin-orbit energies become large. Cotton and Wilkinson<sup>5</sup> discuss the relationship of spin-orbit coupling to magnetic properties. If the spin-orbit splitting becomes large as compared to thermal energy, paramagnetic effects can be largely suppressed. Another very important consequence is the breakdown of spin selection rules and the enhancement of rates of singlet-triplet interconversion. This is well-known to those working with heavy elements but

(28) B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules", Pergamon Press, Oxford, 1970.

is sometimes ignored by others. The very strong spectral line of mercury at 2537 Å is a "spin-forbidden"  $^3P_1 \rightarrow ^1S_0$  transition. The intensity of this line is a vivid reminder that spin is not separately quantized in heavy atoms.

The magnetic properties and the related splittings in the spectra of many compounds involving heavy atoms were initially interpreted with appropriate consideration of spin-orbit energies. For example, Moffitt et al.<sup>29</sup> showed that the spectra of the molecules ReF<sub>6</sub> to PtF<sub>6</sub> are closer to  $j-j$  coupling than to  $L-S$  coupling but that ligand field effects are even more important. Since most of the literature presently gives full consideration to the relativistic (spin-orbit) effects for these properties, there is no need for further comment here.

### Summary

While spin-orbit effects have been recognized in interpreting magnetic properties of molecules containing heavy atoms, more elaborate calculations are required to establish the contribution of relativistic terms to bond energies, ionization potentials, and various chemical properties. Relativistic quantum mechanical calculations have now been made for atoms and for a few molecules, and one can show that many of the anomalous departures from periodic table trends for heavy atoms can be attributed to relativistic effects.

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(29) W. Moffitt, G. L. Goodman, M. Fred, and B. Weinstock, *Mol. Phys.*, **2**, 109 (1959); see also B. Weinstock, *Chem. Eng. News*, **42**, 86 (Sept 21, 1964).

## Relativity and the Periodic System of Elements

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We live in a world with a finite speed of light,  $c$ . Yet, most of the existing theoretical chemistry refers to an

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imaginary world where  $c$  would be infinite. In the following we define relativistic effects as the difference between these two cases. The essential point of the present Account is that these effects seem to explain some of the most conspicuous chemical anomalies in the latter half of the periodic system.

Examples of these are: Why is gold yellow and noble? Indeed, why is it different from silver at all? Why is mercury a liquid? What causes its strong tendency for two-coordination? Why is the mercurous ion so stable? How can one explain the valency change from III for

indium to I for thallium or from IV for tin to II for lead?

### The Three Main Effects

**Methods of Calculation.** The basis for relativistic quantum chemistry is the relativistic one-electron equation of Dirac.<sup>1</sup> For one electron in potential  $V(\mathbf{r})$  it reads

$$h\psi = (\alpha\mathbf{p} + \beta mc^2 + eV(\mathbf{r}))\psi = E\psi \quad (1)$$

When the analogous solutions  $\psi_i$  in the many-electron field are used as the one-electron states in a single Slater determinant

$$\Psi = |\psi_1(1)\psi_2(2) \dots \psi_N(N)| \quad (2)$$

with the Hamiltonian

$$H = \sum_i h_i + \sum_{i>j} \frac{1}{r_{ij}} \quad (3)$$

one gets the relativistic Hartree-Fock or Dirac-Fock equations<sup>2,3</sup>

$$H\Psi = E\Psi \quad (4)$$

Nonrelativistic results may be obtained from them by giving  $c$  a very high value instead of its true value, 137.036 au (atomic units, the system of units where  $e = m_e = \hbar = 1$ ). Solutions of eq 4 for all atoms,  $1 \leq Z \leq 120$ , are given by Desclaux.<sup>4</sup>

Many of the points discussed in this Account came up during our own Dirac-Fock one-center expansion calculations.<sup>5-11</sup> The other contributions to relativistic molecular calculations include approaches like the local density discrete variational method,<sup>12-14</sup> the Dirac-Slater multiple scattering method,<sup>15-17</sup> various relativistic pseudopotential methods,<sup>18-21</sup> or extended Hückel type methods,<sup>22</sup> including the "relativistically parametrized extended Hückel theory" (REX)<sup>23a,b</sup> A

(1) P. A. M. Dirac, *Proc. R. Soc. London*, **117**, 610 (1928).

(2) B. Swirles, *Proc. R. Soc. London, Ser. A*, **152**, 625 (1935).

(3) I. P. Grant, *Proc. R. Soc. London, Ser. A*, **262**, 555 (1961).

(4) J. P. Desclaux, *At. Data Nucl. Data Tables*, **12**, 311 (1973).

(5) J. P. Desclaux and P. Pyykkö, *Chem. Phys. Lett.*, **29**, 534 (1974).

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(7) P. Pyykkö and J. P. Desclaux, *Chem. Phys. Lett.*, **42**, 545 (1976).

(8) P. Pyykkö and J. P. Desclaux, *Nature (London)*, **266**, 336 (1977).

(9) P. Pyykkö and J. P. Desclaux, *Chem. Phys. Lett.*, **50**, 503 (1977).

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(11) (a) P. Pyykkö, *J. Chem. Soc., Faraday Trans. 2*, in press; (b) P. Pyykkö, *Phys. Scripta*, in press.

(12) A. Rosén and D. E. Ellis, *Chem. Phys. Lett.*, **27**, 595 (1974).

(13) A. Rosén and D. E. Ellis, *J. Chem. Phys.*, **62**, 3039 (1975).

(14) D. E. Ellis and A. Rosén, *Z. Phys.*, **A283**, 3 (1977).

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(16) R. P. Messmer, D. R. Salahub, K. H. Johnson, and C. Y. Yang, *Chem. Lett.*, **51**, 84 (1977).

(17) C. Y. Yang, K. H. Johnson, and J. A. Horsley, *J. Chem. Phys.*, **68**, 1001 (1978).

(18) (a) G. Das and A. C. Wahl, *J. Chem. Phys.*, **64**, 4672 (1976); (b) *ibid.*, **69**, 53 (1978).

(19) P. J. Hay, W. R. Wadt, L. R. Kahn, and F. W. Bobrowicz, *J. Chem. Phys.*, **69**, 984 (1978).

(20) (a) S. N. Datta, C. S. Ewig, and J. R. Van Wazer, *Chem. Phys. Lett.*, **57**, 83 (1978); (b) H. Basch and S. Topiol, to be published.

(21) Y. S. Lee, W. C. Ermler, K. S. Pitzer, and A. D. McLean, *J. Chem. Phys.*, **70**, 288 (1979).

(22) R. Manne, K. Wittel, and B. S. Mohanty, *Mol. Phys.*, **29**, 485 (1975).

more complete bibliography is given by Pyykkö,<sup>23c</sup> by Grant,<sup>23d</sup> and in two books in preparation.<sup>23e</sup>

**The Speed of Light as a Limiting Speed.** A feeling for the main relativistic effects may be obtained from simple order-of-magnitude estimates. One of the starting points of the special theory of relativity was that it is impossible to accelerate particles to speeds higher than  $c$ . This follows from the mass increase

$$m = m_0/\sqrt{1 - (v/c)^2} \quad (5)$$

For  $v = c$  the mass  $m$  would become infinite. The average radial velocity of the electrons in the 1s shell of an element is roughly

$$\langle v_r \rangle = Z \text{ au} \quad (6)$$

Thus for mercury,  $Z = 80$ , the average  $v/c$  is of the order  $Z\alpha = 80/137 = 0.58$ .

**Effect 1: The Relativistic Contraction.** One reckons by eq 5, for the 1s electrons of Hg, that the average mass is  $m \approx 1.2m_0$ . Because the Bohr radius contains the mass in the denominator,

$$a_0 = 4\pi\epsilon_0\hbar^2/mZe^2 \quad (7)$$

the relativistic average radius is expected to be about 20% smaller than the nonrelativistic one. All the other s shells, up to the valence shell, contract roughly as much because their electron speeds near the nucleus are comparable and the contraction of the inner part of the wave function pulls in the outer tails. The p electrons contract as well. The magnitude of the contraction of the  $p_{1/2}$  subshell (see below) is comparable to that of  $s_{1/2}$ . The  $p_{3/2}$  subshell contracts much less.

**Effect 2: The Spin-Orbit Splitting.** In a relativistic treatment neither the orbital angular momentum  $l$  nor the spin angular momentum  $s$  of an electron are "good" quantum numbers, but the vector sum

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \quad (8)$$

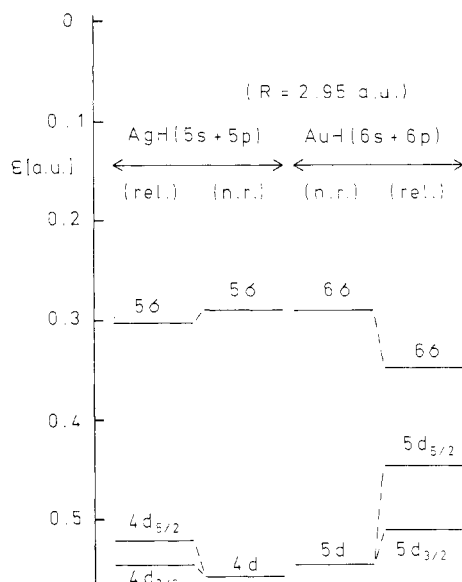
still is. Thus we get for a p electron,  $l = 1$ , the two possible values  $j = 1/2$  and  $j = 3/2$ , denoted as  $p_{1/2}$  and  $p_{3/2}$ , etc. The energetic splitting between these two  $j$  values is a relativistic effect and may rise up to a few electronvolts for the valence electrons of the heaviest elements.

**Effect 3: The Relativistic Self-Consistent Expansion.** The d and f electrons have high angular momenta and seldom descend to the neighborhood of the nucleus where they would reach high velocities. Their main relativistic effects are therefore indirect: because the s and p atomic orbitals (AO's), both inside and outside the d and f AO's, have contracted, they screen the nuclear attraction more efficiently. Therefore the d AO's and the f AO's see a weaker attraction, expand radially, and are destabilized energetically.

Effects 1 and 2 were first noted by Sommerfeld<sup>24</sup> in 1916. Effect 3 was first observed by Mayers<sup>25</sup> and by

(23) (a) L. L. Lohr, Jr., and P. Pyykkö, *Chem. Phys. Lett.*, **62**, 333 (1979); (b) P. Pyykkö and L. L. Lohr, Jr., to be published; (c) P. Pyykkö, *Adv. Quantum Chem.*, **11**, 353 (1978); (d) the atomic calculations were reviewed by I. P. Grant, *Adv. Phys.*, **19**, 747 (1970); (e) two forthcoming books: I. P. Grant, "Relativistic Theory of Atomic Structure", Oxford University Press, Oxford, to be published, and J. P. Desclaux and P. Pyykkö, "Relativistic Theory of Atoms and Molecules", Pergamon Press, Oxford, to be published.

(24) A. Sommerfeld, *Ann. Phys.*, **51**, 1 (1916) (see p 55).



**Figure 1.** The valence orbital energies of the diatomic molecules AgH and AuH from relativistic and nonrelativistic Hartree-Fock one-center expansion calculations. The nonrelativistic ones are very similar, while the relativistic ones are not.<sup>6</sup>

Boyd, Larson, and Waber.<sup>26</sup> The Oxford group<sup>27</sup> has recently pointed out that the contraction, effect 1, is a direct effect, even for the 6s valence electron of Au or the 6p<sub>1/2</sub> one of Tl. For the 6p<sub>3/2</sub> electron of Tl, the indirect relativistic effects from the other shells are comparable with the direct ones.

**The Shell-Structure Expansion.** In addition to these relativistic effects, there are nonrelativistic trends due to the filling of the different electron shells and the different number of nodes in them. Atoms usually become larger when going down a column of the periodic table, although the valence orbital energies,  $\epsilon$ , remain comparable. An order-of-magnitude estimate<sup>28</sup> for this trend may be obtained from the classical turning point,  $r_t$ , of a hydrogen-like atom. At this point, for s states,

$$\epsilon = -\frac{1}{2}(Z/n)^2 = V(r_t) = -Z/r_t \quad (9)$$

Keeping  $Z/n$  constant for a constant  $\epsilon(n)$ , we find the proportionality

$$r_t \propto n \quad (10)$$

Thus the shell-structure expansion is less pronounced for large  $n$ , which makes it easier for relativity to become the dominant trend.

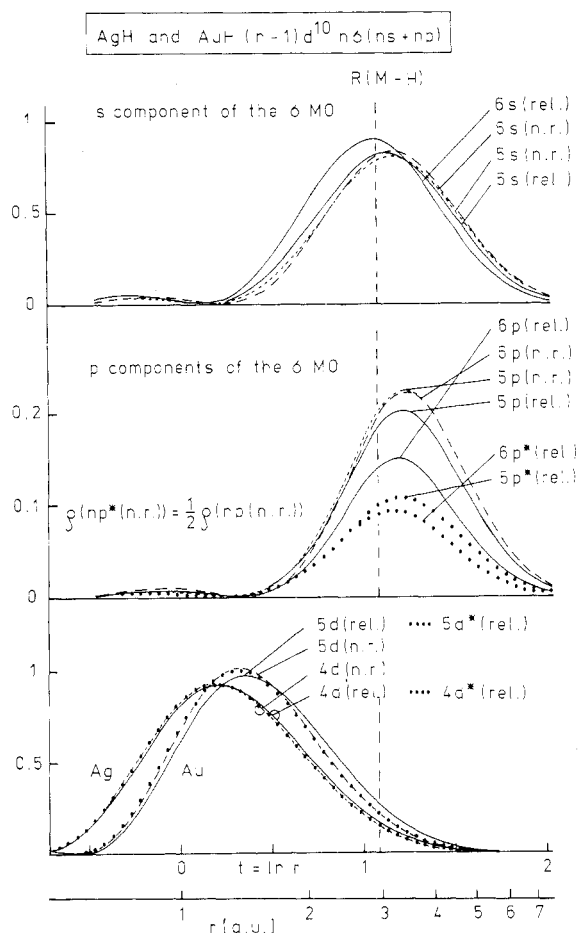
Superimposed on this monotonic shell-structure expansion, the groups 1B, 2B, and 3A-7A exhibit an M-shaped zigzag behavior or "alternation effect"<sup>28b</sup> along a column, with large ionization energies and small heats of formation for oxides for rows 4 and 6. Biron<sup>28c</sup> discussed this effect extensively in 1915, calling it "secondary periodicity". It was attributed by Shchukarev<sup>28d</sup> to partial screening of the nuclear attraction, seen by the valence s and p electrons, by the

(25) D. F. Mayers, *Proc. R. Soc. London, Ser. A*, **241**, 93 (1957).

(26) R. G. Boyd, A. C. Larson, and J. T. Waber, *Phys. Rev.*, **129**, 1629 (1963).

(27) S. J. Rose, I. P. Grant, and N. C. Pyper, *J. Phys. B: At. Mol. Phys.*, **11**, 1171 (1978).

(28) L. L. Lohr, Jr., personal communication; (b) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry", Oxford University Press, Oxford, 1965, Chapters 18.4 and 20; (c) E. V. Biron, *Zh. Russ. Fiz.-Khim. Obshch.*, **47**, 964 (1915); (d) S. A. Shchukarev, *Zh. Obshch. Khim.*, **24**, 581 (1954); (e) P. Pyykkö, to be published.



**Figure 2.** The radial electron distributions of the diatomic molecules AgH and AuH from relativistic (full curves and dotted curves) and nonrelativistic (dashed curves) Hartree-Fock one-center expansion calculations. The difference between Ag and Au is mainly a relativistic effect for the valence s and p shells and mainly a nonrelativistic one for the d shells. The vertical line gives the bond distance.

underlying d<sup>10</sup> or f<sup>14</sup> shells. We<sup>29e</sup> have recently confirmed this explanation by atomic calculations on "pseudo-Se" ( $Z = 24$ , 3d<sup>0</sup>) and "pseudo-Po" ( $Z = 70$ , 4f<sup>0</sup>). For Po, relativistic effects are comparable to this "transition-metal contraction".

### A Case Study: Silver and Gold

The chemical difference between silver and gold has received a great deal of attention during the history of chemistry.<sup>29</sup> It seems to be mainly a relativistic effect.<sup>6</sup>

The nonrelativistic orbital energies of the free Ag and Au atoms or of their diatomic hydrides (Figure 1) are strikingly similar. The spectroscopic properties of AgH and AuH are well-known.<sup>30a</sup> The relativistic effects push the s and p AO's down in energy (effect 1) and the d AO's up (effect 3). Moreover, the d AO's suffer a spin-orbit splitting (effect 2). All three effects are much larger for Au than for Ag. From the radial electron distributions in Figure 2, it is evident that the Ag-Au difference is mainly caused by relativistic effects for the s and the p. For the d, the main difference is due to nonrelativistic shell-structure effects, although the relativistic expansion increases it.

(29) E. von Meyer, "Geschichte der Chemie", von Weit, Leipzig, 1905.

(30) (a) G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, 1950; (b) "Handbook of Chemistry and Physics", 57th ed., CRC Press, Cleveland, OH, 1976.

The relativistic contraction of the Au 6s shell qualitatively explains the shorter and stronger covalent bonds, as well as the larger ionization potential<sup>30b</sup> and electron affinity<sup>31a</sup> of gold. The relativistic destabilization of the Au 5d shell qualitatively explains the trivalency and pentavalency of gold. Besides this energetic effect, the larger radial extension of the 5d shell may also play a role (see Figure 2).

Finally, the yellow color of gold is probably also a relativistic effect. It is attributed to the 5d-to-Fermi level transitions<sup>32a</sup> which set in around 2.3 eV in Au. Thus gold reflects the red and yellow and strongly absorbs the blue and violet. As seen from Figure 1, the 4d-5s distance of Ag is much larger, due to weaker relativistic effects, and in fact, Ag shows the analogous absorption in the UV, above 3.5 eV. The nonrelativistic electronic band structures of the two metals are very similar.<sup>32b</sup> The band structure calculations of Christensen and Seraphin<sup>32c</sup> also support this interpretation of the color of gold. While the relativistic 5d-to-(6s + 6p) interband absorption is calculated to occur at  $h\nu = 2.38$  eV, in the middle of the visible range, in good agreement with experiment, the corresponding nonrelativistic band gaps are much larger.

Similarly, it is interesting that the nonrelativistic orbital energies<sup>16</sup> of Pd and Pt clusters are very similar, while the relativistic ones are not.

The traditional explanation for the smaller size of Au is the lanthanoid contraction. As seen from Figure 1 and 2, its effect is only sufficient to cancel the shell-structure expansion, to make Au (nonrelativistic) similar to Ag (nonrelativistic).

The relativistic contraction of the half-filled valence s AO makes Au<sub>2</sub> much more strongly bound than Ag<sub>2</sub>. Inasmuch as Hg<sub>2</sub><sup>2+</sup> and Cd<sub>2</sub><sup>2+</sup> are isoelectronic with these two molecules, the remarkable stability of the mercurous ion can also be understood.<sup>23c</sup>

According to the relativistic pseudopotential calculation of Lee et al.,<sup>21</sup> the relativistic increase of the Au<sub>2</sub> dissociation energy is about 1 eV out of the total experimental  $D_e$  of 2.34 eV.

We also may follow the relativistic contraction of the 6s shell of Au, (5d)<sup>10</sup>(6s)<sup>1</sup>, from the point of view of the 6s hole. It is now so deep-lying in the atom and filling it feels so good that gold is "almost a halogen". The compound CsAu is a semiconductor and thus exhibits the oxidation state Au(-I). No corresponding silver compound is known. The analogies between iodine and gold were pointed out already by Nyholm.<sup>33</sup>

### Other Consequences of the Contraction, Effect 1

**Groups 1A and 2A.** Fricke and Waber<sup>34</sup> observed that the relativistic contraction of the valence ns shell overtakes the shell-structure expansion after Cs or Ba. Thus Cs is the largest and most easily ionized<sup>30b</sup> atom in Nature. In the more ionic compounds the crystal radius is determined by the (n - 1)p shell with much smaller relativistic effects, and the ionic radius of Ra<sup>2+</sup> is still some 6-9 pm larger<sup>35</sup> than that of Ba<sup>2+</sup>. Simi-

larly, the bond length of the model system RaH<sub>2</sub> is calculated to be larger than that of BaH<sub>2</sub> and the diatomic RaH<sup>+</sup> larger than BaH<sup>+</sup> with, in fact, very small relativistic effects due to strong spd hybridization, at least in the Dirac-Fock one-center method used.<sup>11</sup>

**Group 2B.** The relativistic contraction of the filled (6s)<sup>2</sup> shell of Hg makes it more inert, "almost a rare gas" or "pseudohelium".<sup>23c</sup> The relativistic interatomic potential  $V(\text{Hg}\dots\text{Hg})$  is estimated to have only 45% of the depth of the nonrelativistic one.<sup>36</sup> To establish definitively why in group 2B Cd is solid but Hg a liquid at room temperature, one would need detailed calculations. Probably, the explanation is relativistic.

Nyholm<sup>37a</sup> explained the dominant two-coordination of Hg by the large 6s-6p separation which favors sp hybridization (50% of p character) rather than sp<sup>3</sup> hybridization (75% of p character). We<sup>11a</sup> pointed out that the nonrelativistic valence ns-*np* separations of Cd and Hg are similar, while relativistic effects increase that of Hg by more than a factor of 2 by pulling down the 6s AO. Thus the two-coordination of mercury in its organometallic compounds may largely be due to effect 1. Cadmium forms both two-coordinate and four-coordinate organometallic compounds. The same explanation applies on systems like AuCl<sub>2</sub><sup>-</sup> or Tl(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>. The complementary mechanism of Orgel<sup>37b</sup> invokes d-s mixing due to a small 5d-6s distance. It may also be largely attributed to the relativistic effects 1 (for 6s) and 3 (for 5d).<sup>11a</sup>

**Bond Lengths.** From the point of view of structural chemistry, the question is whether relativistic effects make the bond lengths larger or smaller and roughly how much. These structural changes reflect the contractions or expansions of the individual atomic orbitals participating in the bond. It is perhaps appropriate to point out that these bond-length contractions are something quite different from the famous relativistic contraction of length or of time.

The Dirac-Fock one-center expansion calculations<sup>5-7,11</sup> suggest that in the hydrides, MH<sub>n</sub>, of the groups 3A, 4A, and 1B the relativistic contraction of the  $R(\text{M}-\text{H})$  bond length

$$C = (R_{\text{nr}} - R_{\text{rel}}) / R_{\text{nr}} \quad (11)$$

behaves roughly as

$$C(\%) = [(10(3)) \times 10^{-4}] Z^2 \quad (12)$$

The absolute contraction of the covalent radius of element Z is (in pm)

$$r(\text{nr}) - r(\text{rel}) \simeq [(17(6)) \times 10^{-4}] Z^2 \quad (13)$$

The contractions for Au<sub>2</sub><sup>21</sup> and H<sub>2</sub><sup>38</sup> are included in this average. Thus the H-H bond of H<sub>2</sub><sup>+</sup> contracts about 0.0016 pm,<sup>38</sup> while the Au-Au bond of Au<sub>2</sub> contracts about 35 pm or 0.35 Å<sup>21</sup> due to relativistic effects. The contraction of Au is anomalously large, in fact as large as could be expected around fermium, Z = 100 (see Figure 4).

(35) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

(36) N. C. Pyyper, I. P. Grant, and R. B. Gerber, *Chem. Phys. Lett.*, **49**, 479 (1977).

(37) (a) R. S. Nyholm, *Proc. Chem. Soc. London*, 273 (1961); (b) L. E. Orgel, *J. Chem. Soc.*, 4186 (1958). The first tetraalkylmercurate(II) compound was reported by H. Schmidbaur, O. Gasser, T. E. Fraser, and E. A. V. Ebsworth, *J. Chem. Soc., Chem. Commun.*, 334 (1977).

(38) S. K. Luke, G. Hunter, R. P. McEachran, and M. Cohen, *J. Chem. Phys.*, **50**, 1644 (1969).

(31) (a) E. C. M. Chen and W. E. Wentworth, *J. Chem. Educ.*, **52**, 486 (1975); (b) J. D. Corbett, *Inorg. Nucl. Chem. Lett.*, **5**, 81 (1969).

(32) (a) K. E. Saeger and J. Rodies, *Gold Bulletin (South Africa)*, **10**, 10 (1977); (b) J. Keller, personal communication; (c) N. E. Christensen and B. O. Seraphin, *Phys. Rev. B*, **4**, 3321 (1971).

(33) C. K. Jørgensen, personal communication, quoting R. S. Nyholm.

(34) B. Fricke and J. T. Waber, *J. Chem. Phys.*, **56**, 3246 (1972).

This bond length contraction is caused by effect 1 of the valence  $s$  and  $p$  shells of the metal  $M$ . The early result<sup>38</sup> for  $H_2^+$ ,  $C = 15$  ppm, roughly agrees with the trend called for by eq 12. Comparable results were obtained for  $AuCl$  and  $HgCl_2$  ( $C = 6.7$  and  $4.9\%$ , respectively)<sup>19</sup> from relativistic pseudopotential calculations. For  $AuH$ , Hay et al.<sup>19</sup> find a  $C$  value of about 14–17% while the Dirac–Fock one-center values<sup>11</sup> are 7 and 9% with and without the  $6p$  AO's in the valence  $6\sigma$  MO, respectively. In this case the atoms are nearly neutral ( $Au^{+0.02}H^{-0.02}$ ) and the one-center result may be too small because the hydrogen atom is described by a linear combination of the  $6s$  and the more weakly contracting  $6p$  AO's on Au.

Actually one must note that neither the bond length contraction  $C$  nor the contractions of the individual AO's are smooth functions of the nuclear charge  $Z$ . In particular, the contraction of the valence  $s$  shell reaches a local maximum around the coinage metals, group 1B (see ref 4, pp 387 and 399, or Figure 4 herein).

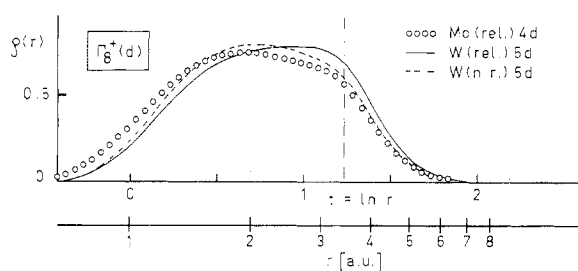
**The Lanthanoid Contraction.** The filling of the  $4f$  shell brings with it a contraction of the  $5p$  and  $6s$  shells, attributed to only partial screening of the increasing nuclear charge by the  $4f$  electrons. The  $4f$  shell itself also contracts for the same reason, its occupants behaving as “transparent brothers” to each other. This “lanthanoid contraction” is also felt in the ionic radii of the  $M^{3+}$  ions or in the calculated bond lengths for the tetrahedral model systems  $CeH_4$  and  $HfH_4$ . These two systems are otherwise isoelectronic, but the former has an empty and the latter a filled  $4f$  shell. A comparison of the calculated relativistic and nonrelativistic bond lengths then suggests that about 14% of the lanthanoid contraction is due to relativistic effects. An inspection of the calculated  $5p$  radii suggests a somewhat smaller relativistic percentage.<sup>10</sup>

### Consequences of the Expansion, Effect 3

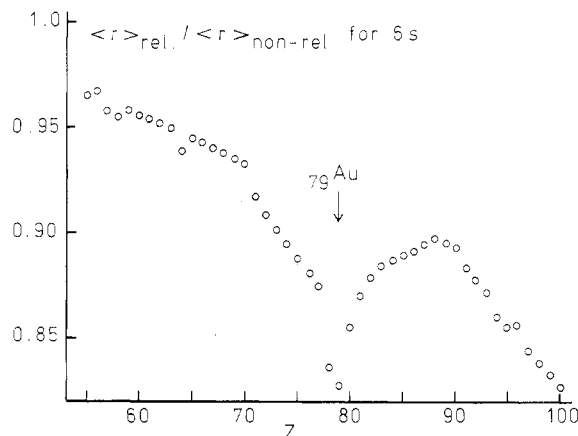
**Group 2A.** Strong  $3d$ ,  $4d$ , or  $5d$  contributions to the bonding of Ca, Sr, and Ba, respectively, were found by Pyykkö.<sup>11</sup> After Ba, the nonrelativistic  $d$  character would increase further for Ra while the relativistic one decreases. The decrease is, however, not very large. Both Ba and Ra have the body-centered cubic structure, typical for a large  $d$  character, while Ca and Sr are face-centered cubic.<sup>39</sup>

**Group 4B.** At this point the alert reader probably begins to suspect that the chemical difference between any fifth-row element and the corresponding sixth-row element might largely be of relativistic origin and that these relativistic effects would always be large for heavy elements. The elements Zr and Hf form an interesting exception.

Zirconium and hafnium are chemically very similar, despite the fact that Hf is a heavy element for which rather large relativistic effects could be expected. Model calculations<sup>9</sup> on the tetrahedral  $ZrH_4$  and  $HfH_4$  give very similar nonrelativistic results. This may be attributed to the traditional reason: the cancellation of the shell-structure expansion by the lanthanoid contraction. The relativistic effects were found to be very small due to a cancellation of effect 1 and effect 3. The valence  $t_2$  MO of  $HfH_4$  can be spanned by either the  $5d$  AO (which expands) or the  $6p$  AO (which



**Figure 3.** The calculated Dirac–Fock radial electron distributions for the  $(4d)^4$  shell in the octahedral model system  $MoH_6$  and the corresponding  $(5d)^4$  shell of  $WH_6$ . The curve for nonrelativistic  $W$  is qualitatively similar to that of  $Mo$  while the curve for relativistic  $W$  is strongly shifted toward the ligands. The vertical dashed line gives the  $M$ – $H$  distance. Reproduced with permission from ref 10. Copyright 1978, North-Holland Publishing Co.



**Figure 4.** The relativistic contraction of the  $6s$  shell in the elements Cs ( $Z = 55$ ) to Fm ( $Z = 100$ ). The numbers are taken from the Dirac–Fock and Hartree–Fock calculations of Desclaux.<sup>4</sup> The contraction increases considerably while the  $4f$  shell is being filled and strikingly when the  $5d$  shell is filled. The pronounced local maximum of the contraction at gold,  $(5d)^{10}(6s)^1$ , makes Au a unique element, even from this point of view. As discussed in the text, the redox nobility of gold is related to this contraction. An equally strong relativistic contraction is not found until reaching fermium,  $Z = 100$ .

contracts). About 50% of both AO's were found in the Dirac–Fock one-center calculation. This suggests that the chemical similarity of Zr and Hf may be due to an anomalous cancellation of relativistic effects.

**A Valency Rule for Heavy Transition Elements.** When going to the right of group 4B, relativity pushes the orbital energies of the  $5d$  AO's above those of the  $4d$  AO's of the previous row. This suggests that the  $5d$  AO's would be more easily available for chemical bonding. The larger radial extension of the  $5d$  AO's will also help. A similar statement can be made, a fortiori, about the  $4f$  and  $5f$  elements. Thus, e.g., Mo forms bromides up to  $MoBr_4$ , while the corresponding  $5d$  element W also forms  $WBr_5$  and  $WBr_6$ . This led us to propose the rule:<sup>23c</sup> *For predominantly ionic compounds of two heavy ( $4d/5d$  or  $4f/5f$ ) transition elements belonging to the same column, the heavier one exhibits the higher valency, with effect 3 as the suggested explanation.* While the empirical facts are well-known, the explanation is probably new. It is supported by our later Dirac–Fock one-center calculations<sup>10</sup> on the octahedral model systems  $MoH_6$  and  $WH_6$  (Figure 3).

Basch and Topiol<sup>20b</sup> similarly found for the diatomic molecule  $PtH$  that the relativistic expansion of the  $5d$

(39) (a) B. Vasvari, A. O. E. Animalu, and V. Heine, *Phys. Rev.*, **154**, 535 (1967); (b) F. Weigel and A. Trinkl, *Radiochim. Acta*, **10**, 78 (1968).

shell actually enhanced its participation in bonding and, in fact, changed the molecular ground state from  $^2\Sigma$  to the observed  $^2\Delta$ .

Reiterating, it appears that the relativistic self-consistent-field expansion, effect 3, of an  $nd$  (or  $5f$ ) atomic orbital may have two diametrically opposed consequences depending on whether the orbital energy of this  $d$  AO is above or below those of the other valence orbitals. In the former case, like the  $6d$  participation to the bonds of radium, effect 3 makes the  $d$  AO energetically less accessible and diminishes its contribution. In the latter case, like the  $5d$  participation to the bonds of tungsten or platinum, effect 3 pushes the  $d$  AO up in energy and outwards in space, diminishing its isolation in the atomic core and increasing its contribution to the bond, thus strengthening the latter.

We found that relativistic effects are needed to make the  $W-H$  bonds as short as the  $Mo-H$  ones and to make the former stronger than the latter.<sup>10</sup>

### Consequences of Spin-Orbit Splitting, Effect 2

**Ionization Potentials.** Fricke, Greiner, and Waber<sup>40</sup> observed that in the  $(np)^k$  series  $I_1$  increases from  $k = 1$  to  $3$  for  $n = 2-5$  but only increases from  $k = 1$  to  $2$  for  $n = 6$ . Thus, due to a partial transition towards  $j,j$  coupling, Pb is to some extent a "rare gas" with the filled shells  $(6s)^2(6p_{1/2})^2$ . The following element, Bi, is in the same sense an "alkali metal" with the electron configuration  $(6s)^2(6p_{1/2})^2(6p_{3/2})^1$ . It has a slightly smaller  $I_1$  and, in fact, also exhibits a valency of one.

In  $j,j$  coupling (see eq 8) the good quantum number for a single electron is  $j$ . The electron shells are classified in terms of  $l$  and  $j$ . The case with  $l = 1$  and  $j = 1/2$  was called  $p_{1/2}$ . In this case the magnetic quantum number  $m_j$  (or the component of  $j$  along a given direction) may assume the two possible values  $+1/2$  and  $-1/2$ . Therefore the  $p_{1/2}$  shell may accommodate two electrons. Similarly, the  $p_{3/2}$  shell may receive up to four electrons with  $m_j$  equal to  $+3/2$ ,  $+1/2$ ,  $-1/2$ , or  $-3/2$ .

Due to the spin-orbit splitting, the  $p_{1/2}$  shell lies below the corresponding  $p_{3/2}$  shell and is therefore filled first.

**Electron Affinities.** The fact that Tl has an anomalously large electron affinity<sup>31a</sup> may be attributed to the stability of the  $(6p_{1/2})^2$  shell. The large electron affinity of Hg<sup>31b</sup> may also be connected to the relativistic contraction of the  $6p_{1/2}$  shell.

**Valency Changes.** The elements B to In are trivalent, while Tl is dominantly monovalent. The ele-

ments C to Sn are quadrivalent, while Pb is dominantly divalent. Three different partial explanations can be given to this change, and two of them ((a) and (c)) are actually relativistic:

(a) Sidgwick's inert pair effect<sup>41</sup> is based on the fact that the  $6s$  electrons have larger binding energies than the corresponding  $5s$  ones. Then the  $6s-6p$  hybridization is energetically less favorable and an  $(6s)^2$  "inert pair" is formed. We are now able to attribute this "relativistic dehybridization"<sup>42</sup> to effect 1.

(b) Drago<sup>43</sup> invokes the shell structure expansion which gives a smaller angular overlap with a given ligand, and therefore a smaller binding energy, which leads to the same dehybridization.

(c) Fricke<sup>44</sup> proposed on the basis of atomic calculations and we<sup>7</sup> on the basis of molecular calculations that the orbitals isolated from bond formation may not necessarily be the  $6s$  but rather the upper, empty, spin-orbit split component  $6p_{3/2}$ . Thus, in a molecule like TlH, we would have, instead of  $p\sigma$  bonding, " $p_{1/2}$  bonding".<sup>7</sup> The relative roles of the three mechanisms (a-c) are so far unknown.

The partial transition towards  $p_{1/2}$  bonding makes the bond weaker. The underlying reasons were first analyzed by Pitzer.<sup>45</sup>

As a historical curiosity we note that these  $j,j$  coupling effects were already used, in a qualitative way, to discuss the various valencies of the halogens by Grimm and Sommerfeld<sup>46</sup> by simply invoking subsequent ionization from the various subshells.

### Concluding Remarks

The chemical difference between the fifth row and the sixth row seems to contain large, if not dominant, relativistic contributions which, however, enter in an individualistic manner for the various columns and their various oxidation states, explaining, for example, both the inertness of Hg and the stability of Hg<sub>2</sub><sup>2+</sup>. These relativistic effects are particularly strong around gold. A detailed understanding of the interplay between relativistic and shell-structure effects will form the impact of relativity on chemistry.

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(42) J. C. Phillips, "Bonds and Bands in Semiconductors", Academic Press, New York, 1973.

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(46) H. G. Grimm and A. Sommerfeld, *Z. Phys.*, **36**, 36 (1926).

(40) B. Fricke, W. Greiner, and J. T. Waber, *Theor. Chim. Acta*, **21**, 235 (1971).