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Relativistic Effects on Chemical Properties

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While it is generally recognized that a rigorous theoretical foundation for chemistry would rest on relativistic quantum theory, the great majority of quantum mechanical calculations of quantities of chemical interest are based on the nonrelativistic Schrödinger equation, or its equivalent, together with the qualitative rules related to spin and the Pauli exclusion principle. If fine structure features are of interest, spin–orbit, spin–spin, and other terms are added as perturbations, but for light atoms these terms yield very small energies that may be of spectroscopic interest but have no effect on most chemical properties.

For very heavy atoms, however, this situation changes. Certain terms which were very small compared to thermal energy for light atoms increase very rapidly with atomic number and become comparable to chemical bond energies for elements in the range gold–bismuth.

The most familiar relativistic property is probably the increase in particle mass as the velocity approaches that of light. It is the s electrons with no orbital angular momentum that approach the nucleus most closely and therefore gain the highest velocity. For these heavy atoms the inner 1s and 2s electrons have average velocities close enough to that of light to have a substantial increase in mass. As a result these electrons spend even more time near the nucleus, have contracted mean radii, and have orbital energies which are increased (more negative). With this contraction of the inner s shells, outer s electrons also get closer to the nucleus and are affected in the same way. The relativistic effects on p, d, and f electrons are more complex and will be discussed below. But the essential result is that calculations based on the Schrödinger equation are not adequate for a discussion of the chemical properties of heavy atoms. Also extrapolations downward in the periodic table for the properties of possible superheavy elements are very hazardous since these relativistic effects increase very rapidly with increase in atomic number.

Table I
Energy Terms for Fourth Group Elements (Electronvolts)

element X	ionization potential	X_2 bond D_0	spin-orbit $^3P_2$-$^3P_0$
C	11.26	6.1	0.005
Si	8.15	3.2	.03
Ge	7.88	2.8	.17
Sn	7.34	2.0	.42
Pb	7.42	1.0	1.32

My principal purpose in this Account is to examine the special or anomalous chemical effects that have been noted for heavy elements in relation to periodic-table trends and to determine the degree to which these are relativistic effects. To the extent that these anomalies are explained in most inorganic chemistry books, they are usually ascribed to the introduction of the 4f shell. It is found that the effects of the 4f shell and the effects of relativity are of comparable magnitude, with the latter becoming more important for elements substantially heavier than the lanthanides.

The mathematical structure of relativistic quantum mechanics[1] is considerably more complex than that of the nonrelativistic theory; hence, one uses fully relativistic theory based on the Dirac equation only when it is needed. For work with elements of intermediate atomic number, there is a well-developed perturbation theory, due largely to Pauli, which allows one to examine the various relativistic terms on the basis of the Schrödinger wavefunctions and to include those corrections which may be significant in a particular situation. But for very heavy elements the validity, or even the convenience, of this perturbation approach is doubtful, and it is better to start with the Dirac equation.

After submitting the initial version of this Account I learned of the Account of Pyykkö and Desclaux[2] which is being published simultaneously. These authors outline the mathematical formulation of relativistic quantum theory, including the Dirac equation; hence the corresponding material has been deleted from the present paper. Also available is a more detailed review by Pyykkö[3] with an extensive bibliography.

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(1) See, for example, H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms", Academic Press, New York, 1957; or I. P. Grant, *Adv. Phys.*, 19, 747 (1970).

(2) P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.*, 12, 271 (1979).

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In a sense the spin of electrons and other particles and the exclusion principle are themselves relativistic effects in that they are integral parts of relativistic quantum theory whereas they are appended as separate postulates in the conventional theory which starts with the Schrödinger equation. But the effects arising from spin alone or from the exclusion principle are not the subject of this Account; indeed they are part of conventional "nonrelativistic" theory. The spin-orbit energy, which is often mentioned as an effect splitting spectral lines, is a relativistic effect in our present sense and is one of those terms which becomes large for heavy elements. Indeed it is convenient to take this spin-orbit energy as a measure of the need to use relativistic theory for chemical phenomena. In Table I the spin-orbit energies are compared with ionization potentials and bond dissociation energies for the fourth group elements.

A chemical bond energy for relatively large atoms is roughly 2 eV (46 kcal or 190 kJ). From Table I we see that the spin-orbit term is small compared to a chemical bond energy for fourth group elements through tin but becomes larger than the bond energy in lead. Also there is an anomalous drop in the bond energy for lead below that of any reasonable extrapolation of the trend from silicon to germanium to tin. This illustrates the hazard in a simple extrapolation for the bond energy of eka-lead, element 114, which is of interest as a possible synthetic superheavy element.[4]

From data such as that in Table I, one can estimate that the perturbation approach starting with nonrelativistic theory will probably suffice through elements such as tin for chemical bonding calculations as well as for spin-orbit energies, but that for heavier elements one should use fully relativistic theory. Experience to date on molecular calculations is in agreement with that estimate.

Let us turn now to a more comprehensive consideration of the anomalous effects that have been noted for heavy elements. Cotton and Wilkinson,[5] in their third edition of "Advanced Inorganic Chemistry", do not mention relativistic effects explicitly, but they do note: (1) the lanthanide contraction, (2) the inert pair effect, (3) the unique properties of gold (as compared to Ag and Cu), of mercury (as compared to Cd and Zn), and of U^{VI}, Np^{VI}, and Pu^{VI} (as compared to the corresponding lanthanides), and (4) the effect on magnetic properties of the large spin-orbit interaction in compounds of Os^{IV}, etc. Let us consider first the role of relativity as compared to other possible factors for (1) through (3). The spin-orbit effect in (4) is purely relativistic, and we shall subsequently comment briefly on it.

We consider first the conclusions that can be drawn from comparisons of relativistic and nonrelativistic calculations for atoms. There are complete tables of self-consistent-field calculations[6-8] yielding orbital energies, radii of the various orbitals, and other properties. Also the orbital energies are approximately related to experimental ionization potentials.[9] Thus it is convenient to use this information concerning the atoms to a maximum extent.

Table II
Lanthanide Contraction: 5p Mean Radii (4p for Yttrium) and Observed Ionic Radii (Å)

	calculated ⟨r⟩				observed ionic radius
	nonrel	av rel	$p_{3/2}$	$p_{1/2}$	
Y	0.778	0.774	0.779	0.763	0.88
La	0.970	0.958	0.971	0.931	1.061
Lu	0.774	0.745	0.764	0.706	0.848

Not very many relativistic calculations have been made, as yet, for the electronic motion in molecules. In a later section a few of these calculations, which yield results of general chemical interest, will be considered, but we make no pretense of giving a complete account of all relativistic calculations on the electronic structure of atoms and molecules.

Conclustions Based on Atomic Properties

In addition to atomic spectral data we have complete tables from Desclaux[6] based on solution of the Dirac equation and yielding orbital energies, radii, and other properties. Comparable nonrelativistic tables are available from several sources.[7,8] Except for s orbitals, where there is no orbital angular momentum, the spin-orbit interaction divides a shell of a given l into subshells with total angular momentum $j = l - {}^1/_2$ and $j = l + {}^1/_2$. Relativistic calculations yield separate energies and radii for each subshell. The difference in energy is just the spin-orbit energy. Where it is appropriate to average the properties of the subshells, they are weighted as $2j + 1$.

Electronic velocities are highest in the region close to the nucleus. Thus it is not surprising that relativistic effects are greatest for s orbitals which have the greatest density near the nucleus and in the direction of decreasing the radius and increasing the ionization potential. The effect on p orbitals is in the same direction, but smaller. These effects on s and p orbitals increase the shielding of the nuclear charge for d and f electrons; hence the net relativistic effect may be reversed, i.e., increased radius and decreased ionization potential.

It is well-known that the radii of the lanthanide ions decrease from La to Lu and that this reduction in radius persists for the following elements. This "lanthanide contraction" is cited as the immediate cause of the near equality of radii (in comparable oxidation states) for Hf and Zr, Ta and Nb, etc., through Au and Ag and possibly further. The underlying cause is commonly stated as the incomplete shielding of the nucleus by the 14 4f electrons; thus a larger effective core charge contracts the 5p, 5d, 6s orbitals. This is the single most important cause of the contraction. But we shall see that the relativistic equation yields smaller radii than the nonrelativistic equation in some cases.

Table II gives both the relativistic and nonrelativistic calculated radii for the 5p shell as well as the experimental ionic radii[5] for lanthanum and lutetium and for comparison also for yttrium (4p shell). One would not

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(3) P. Pyykkö, *Adv. Quantum Chem.*, 11, 353 (1978).

(4) G. T. Seaborg, W. Loveland, and D. J. Morrissey, *Science*, **203**, 711 (1979).

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, New York, 1972.

(6) J. P. Desclaux, *Atom. Data Nucl. Data*, **12**, 311 (1973).

(7) J. B. Mann, Los Alamos Laboratory Reports LA-3690 (1967) and LA-3691 (1968).

(8) C. Froese Fisher, *Atom. Data*, 4, 301 (1972); *Atom. Data Nucl. Data*, **12**, 87 (1973).

(9) C. E. Moore, "Atomic Energy Levels", NBS Circular No. 467, Vol. I-III, U.S. Government Printing Office, Washington, D.C., revised 1971.

Table III
Radii (⟨r⟩, Å) and Weighted Averages for Relativistic 5d and 6p

	pseudoatom nonrelativistic			real atom nonrelativistic			real atom relativistic		
	5d	6s	6p	5d	6s	6p	5d	6s	6p
Hf	1.325	2.484		1.179	2.153		1.263	1.955	
Re	1.076	2.231		0.952	1.955		0.992	1.734	
Au	0.912	2.235		0.817	1.958		0.839	1.620	
Hg	0.849	1.984		0.758	1.761		0.779	1.515	
Tl		1.762	2.245		1.570	2.078		1.365	2.036
Pb		1.613	1.986		1.442	1.829		1.266	1.783
Bi		1.499	1.805		1.373	1.660		1.187	1.614

Table IV
Calculated Orbital Energies and Experimental Ionization Potentials in eV for Valence Shell Electrons

	$s_{1/2}$	$d_{5/2}$		$d_{3/2}$
Au, exptl	9.22	11.22		12.81
calcd relativ	7.94	11.66		13.43
rel wt av	7.94		12.37	
nonrelativ	6.01		14.17	
pseudoatom	5.18		14.62	
Ag, exptl	7.58	12.51		13.18
calcd relativ	6.45	13.64		14.31
rel wt av	6.45		13.91	
nonrelativ	5.99		14.62	

expect that exact agreement of the experimental ionic radius with the mean value of r for the outer shell of the ion, but there should be a close relationship of relative values. In fact the ionic radius exceeds the average relativistic radius by 0.10_3 Å in all cases. The ionic radius of lutetium is significantly less than that of yttrium. It is also apparent that there is a relativistic contraction which is trivial for yttrium, small for lanthanum, but significant for lutetium. While the relativistic contribution to the total contraction from La to Lu is only about 10%, it is the relativistic effect that reduces the radius of Lu significantly below that for yttrium.

In order to measure the effect of the 4f shell for elements following the lanthanides, nonrelativistic calculations were made[10] for pseudoatoms in which the nuclear charge was reduced by 14 units and the 4f orbitals were deleted. These results are compared with the nonrelativistic and the relativistic results for the real atoms in Tables III–V. For the radius of the 6s orbital the contraction caused by the 4f shell decreases through the series Hf to Bi from 0.33 to 0.13 Å, while the relativistic effect remains about constant at 0.2 Å. Thus, while both effects have the same general magnitude and the same direction, the relativistic effect becomes the more important for the heavier elements. In the case of the 5d orbitals, however, the relativistic effect is in the opposite direction; the 4f shell contracts the 5d orbital, but relativistic effects expand it. From Tl on, the 6p orbitals begin to be occupied and one finds that the effects on the 6p radii are similar to those on the 6s orbital but of decreased magnitude.

Table IV gives energy values for the valence orbitals in gold and silver. The orbital energies calculated on a self-consistent-field basis are only rough approximations to the ionization potentials because electron correlation and relaxation effects are omitted. But with these factors considered, the relativistic values agree well with experiment. Now comparing gold with silver,

Table V
The Inert Pair Effect: Orbital Energies for Ge, Sn, and Pb (eV)

element	Ge	Sn	Pb
s, relativ	15.52	13.88	15.41
s, nonrel	15.16	13.04	12.49
p, wt av rel	7.29	6.71	6.48
p, nonrel	7.33	6.76	6.52
$\Delta\epsilon$, relativ	8.23	7.17	8.93
$\Delta\epsilon$, nonrel	7.83	6.28	5.97
$\Delta\epsilon$, pseudoatom	-	-	4.78

the s electron is more tightly bound in gold than in silver by 1.5 eV, whereas the $d_{5/2}$ electrons are more loosely bound in gold by about the same amount. But within about 0.5 eV the nonrelativistic values for gold or pseudogold are the same as those for silver where relativistic effects are not very large. Thus this large shift toward more strongly bound s and more loosely bound d electrons is primarily a relativistic effect. But these shifts explain very well the differences in chemical behavior. With the high ionization potential for the 6s electron even in the large atom, gold is very difficult to oxidize. But in compounds it forms several strong covalent bonds since 5d orbitals can be involved as well as 6s and 6p. Not only is the difference in energy between d and s orbitals smaller in gold than in silver but the differences in radii are smaller also.

This tendency toward strong covalent bonds is also shown in the diatomic molecule Au_2 whose dissociation energy,[11] 2.29 eV, exceeds that of either Ag_2 (1.65 eV) or Cu_2 (1.95 eV). Also note the trend in D_0 down from Cu_2 to Ag_2, which is a normal pattern, and then anomalously up to Au_2. An extensive theoretical study has been made[12] for Au_2 which is discussed below.

The electron affinities of these atoms are[13] Cu 1.226 eV, Ag 1.202 eV, and Au 2.308_6 eV; again the anomaly for gold is striking and is understandable from the relativistic effect in contracting the 6s orbital and making it more strongly bound. The compounds CsAu and RbAu are unusual in being nonmetallic semiconductors[14] with the CsCl structure. They are presumably based on an ionic M^+Au^- model, and the high electron affinity of gold is essential to their nonmetallic character.

In the case of mercury the combined relativistic and 4f-shell effect contracts the 6s orbital and strengthens

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[10] P. S. Bagus, Y. S. Lee, and K. S. Pitzer, *Chem. Phys. Lett.*, **33**, 408 (1975).

[11] K. A. Gingerich, *J. Cryst. Growth*, **9**, 31 (1971); J. Kordis, K. A. Gingerich, and R. J. Seyse, *J. Chem. Phys.*, **61**, 5114 (1974).

[12] Y. S. Lee, W. C. Ermler, K. S. Pitzer, and A. D. McLean, *J. Chem. Phys.*, **70**, 288 (1979); W. C. Ermler, Y. S. Lee, and K. S. Pitzer, *ibid.*, **70**, 293 (1979).

[13] H. Hotop, R. A. Bennett, and W. C. Lineberger, *J. Chem. Phys.*, **58**, 2373 (1973); H. Hotop and W. C. Lineberger, *ibid.*, **58**, 2379 (1973).

[14] W. E. Spicer, A. H. Sommer, and J. G. White, *Phys. Rev.*, **115**, 57 (1959).

Table VI
Valence Orbital Energies (eV) and Radii (Å) for Uranium

	relativ wt av	nonrelativ
ϵ, 5f	9.01	17.26
ϵ, 6d	5.09	7.25
ϵ, 7s	5.51	4.54
$\langle r \rangle$, 5f	0.76	0.67
$\langle r \rangle$, 6d	1.71	1.52
$\langle r \rangle$, 7s	2.30	2.67

its bonding capacity, as was the case in gold. Thus mercury is a more noble metal than zinc or cadmium and its compounds show stronger covalent bonding. The unexpected volatility of mercury arises from the increase in 6s to 6p promotion energy as compared to zinc and cadmium. The unusual dimeric, dipositive ion Hg_2^{2+} is isoelectronic with Au_2, and we have already noted the anomaly in the strength of the bond in Au_2 which will be shown later to be primarily of relativistic origin. The 5d orbitals play a lesser and the 6p orbitals a greater role in mercury than in gold; the relativistic and 4f-shell effects on radii are shown in Table III. In summary, the anomalous properties of mercury arise from the sum of relativistic and 4f-shell contributions which are of comparable magnitude and reinforce one another in most respects.

The appearance of compounds, primarily in groups 4 through 7, with oxidation number two less than the group number is ascribed to an "inert pair" of s electrons. This effect is enhanced for the 6s, 6p valence shell and is extended to thallium in group 3. Thus the energy required to remove the 6s pair of electrons is much greater for Tl, Pb, and Bi than for the 5s pair in In, Sn, and Sb. The pertinent atomic orbital energies for Ge, Sn, and Pb are given in Table V. On a nonrelativistic basis, even with the effect of the 4f shell, all of the energies decrease along this sequence and no grossly anomalous trend is indicated. But on a relativistic basis, the s electron in Pb is bound as strongly as in Ge and much more than in Sn, while the normal trend is maintained for the weighted average for the p electrons. Thus the difference in binding for s as compared to p electrons shows a very anomalous trend from Sn to Pb. Although the 4f shell effect is in the same direction, as indicated by the value for pseudolead, the major part of the anomaly arises from relativity in this case. The data for the third or fifth group show the same pattern.

There is also an enhanced inert pair effect for the elements Ge through Br as compared to those of the elements in the rows above and below, but this is not a relativistic effect; rather it is associated with the introduction of the first d shell. Just as in the case of the 4f shell in the lanthanides, the shielding of 4s and 4p electrons by the 3d shell is incomplete and less complete for s than for p orbitals. Hence the orbital energies are increased more for 4s than for 4p and the inert pair effect is enhanced in relation to expectations related in part to elements Si through Cl.

Table VII
Dirac Atomic Orbitals[a]

$s_{1/2}$, $m = +^1/_2$ $\begin{bmatrix} g(r) \\ 0 \\ f(r)\cos\theta \\ f(r)\sin\theta\ e^{i\phi} \end{bmatrix}$	$s_{1/2}$, $m = -^1/_2$ $\begin{bmatrix} 0 \\ g(r) \\ f(r)\sin\theta\ e^{-i\phi} \\ -f(r)\cos\theta \end{bmatrix}$
$p_{1/2}$, $m = +^1/_2$ $\begin{bmatrix} g(r)\cos\theta \\ g(r)\sin\theta\ e^{i\phi} \\ f(r) \\ 0 \end{bmatrix}$	$p_{1/2}$, $m = -^1/_2$ $\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ -g(r)\cos\theta \\ 0 \\ f(r) \end{bmatrix}$
$p_{3/2}$, $m = +^3/_2$ $\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ 0 \\ f(r)\sin\theta\cos\theta\ e^{i\phi} \\ f(r)\sin^2\theta\ e^{2i\phi} \end{bmatrix}$	$p_{3/2}$, $m = -^3/_2$ $\begin{bmatrix} 0 \\ g(r)\sin\theta\ e^{-i\phi} \\ f(r)\sin^2\theta\ e^{-2i\phi} \\ -f(r)\sin\theta\cos\theta\ e^{-i\phi} \end{bmatrix}$
$p_{3/2}$, $m = +^1/_2$ $\begin{bmatrix} 2g(r)\cos\theta \\ -g(r)\sin\theta\ e^{i\phi} \\ f(r)(\cos^2\theta - ^1/_3 \\ f(r)\sin\theta\cos\theta\ e^{i\phi} \end{bmatrix}$	$p_{3/2}$, $m = -^1/_2$ $\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ 2g(r)\cos\theta \\ f(r)\sin\theta\cos\theta\ e^{-i\phi} \\ -f(r)(\cos^2\theta - ^1/_3 \end{bmatrix}$

[a] The angular factors are shown explicitly; other factors are included in $g(r)$ and $f(r)$ in each case.

In various discussions[15,16] of the bonding in the uranyl ion, it is suggested that this unique ion has its great stability because 5f, 6d, 7s, and 7p orbitals can all contribute to the remarkably short and strong U–O bonds. Clearly the mean radius of the 5f orbital is much less than that for the others, but in contrast to the 4f orbital, the 5f has a radial node and has significant amplitude at radii much beyond the average. From Table VI it is clear that relativistic effects substantially narrow the ranges of orbital energies and radii from 5f through 7s. Thus it is reasonable to conclude that special properties of oxidation state VI for U, Np, and Pu arise at least in large part because of the relativistic effects in making 7s (and 7p) orbitals more compact and strongly bound while making 5f orbitals larger and much more loosely bound.

We have now shown that most of the anomalous properties of various heavy elements are to be ascribed in substantial part to relativistic effects and that this conclusion can be based on simple arguments from atomic radii and orbital energies (or ionization potentials). In a few situations it is important, however, to recognize differences in the bonding characteristics of relativistic orbitals, especially p orbitals.

Bonding Characteristics of Relativistic Orbitals

While Schrödinger wavefunctions are ordinary scalar functions, Dirac orbitals[1,17] are fourth-order vectors. The electron probability density is given by the sum of the squares (in absolute magnitude) of the four components. Two of these components vanish in the nonrelativistic limit $c \rightarrow \infty$; these are called "small components" and are always very small in the outer portion of an atom but may become important near the nucleus. The other two "large components" can be thought to correspond to the Schrödinger wavefunctions for + and − spin, respectively, and it is these functions that must be considered in estimating the bonding characteristics.

Powell[17] has given a simple and clear description of relativistic orbitals for atoms where various properties are discussed. The angular properties of orbitals are especially important for chemical bonding, and these are shown for $s_{1/2}$, $p_{1/2}$, and $p_{3/2}$ orbitals in Table VII.

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[15] R. E. Connick and Z. Z. Hugus, Jr., *J. Am. Chem. Soc.*, 74, 6012 (1952).

[16] C. Y. Yang, K. H. Johnson, and J. A. Horsley, *J. Chem. Phys.*, 68, 1001 (1978), and references cited therein.

[17] R. E. Powell, *J. Chem. Educ.*, 45, 558 (1968).

Here various factors are included within the functions $g(r)$ and $f(r)$ which are eigenfunctions of the radial equations for the particular atom and principal quantum number. The large components are listed first with the factor $g(r)$; the small components in third and fourth places with the factor $f(r)$.

As one can see from Table VII, the angular properties of s orbitals are unchanged by relativity. The large components have no angular dependence, i.e., are spherical, and only the first or the second component is non-zero. Thus they can form strong bonds in any direction. The only significant relativistic effect on s orbitals is the quantitative change in $g(r)$ whereby they are contracted and more tightly bound. This increases the strength of bonds based on s orbitals.

In contrast, there are profound differences in angular properties for those relativistic p orbitals with z component of angular momentum $m = \pm{}^1/_2$. Both large components are non-zero, and one component has the angular dependence of a pσ orbital whereas the other has that of a pπ orbital. If one forms a diatomic molecular orbital from $p_{1/2}$ atomic orbitals for each atom with signs appropriate for σ bonding, then the other components yield π antibonding. More exactly, if the $p_{1/2}$ orbitals are combined with g symmetry one has one-third σ-bond and two-thirds π-antibond character. Correspondingly, the combination with u symmetry yields one-third σ-antibond and two-thirds π-bond character. Thus $p_{1/2}$ orbitals do not form strong bonds. By taking linear combinations of $p_{1/2}$ and $p_{3/2}$ orbitals, the angular and bonding characteristics of Schrödinger p orbitals can be regained, but this requires substantial promotion energy in many cases.

This relativistic effect for p bonding should be most prominent for Tl_2 where the atom has a single $p_{1/2}$ valence electron. Tl_2 is very weakly bound; indeed its bond energy is still uncertain.[18]

In TlH this effect will be less severe since the hydrogen contributes an s orbital to the bond. With negligible π interaction from the hydrogen, the π-antibonding effect is unimportant, and it is only the reduced σ-bonding effect of a $p_{1/2}$ orbital (as compared to a nonrelativistic p orbital) that remains.

In some exploratory calculations[19] I made the very crude assumption of full promotion of $p_{1/2}$ electrons or $p_{3/2}$ vacancies to the nonrelativistic ${}^1/_3(p_{1/2}) + {}^2/_3(p_{3/2})$ combinations for optimum bonding. Of course, in reality the bonding molecular orbitals will involve a compromise with partial promotion and somewhat weaker bonding than would correspond to the ${}^1/_3(p_{1/2}) + {}^2/_3(p_{3/2})$ combination, but as yet there is no simple method of estimation for the intermediate state. More complex calculations[20,21] of the types discussed in the next section indicate that the proportion of $p_{1/2}$ and $p_{3/2}$ participation in TlH is about 60% $p_{1/2}$ and 40% $p_{3/2}$. This is evidently a compromise between the 100% $p_{1/2}$ for minimum energy of the Tl atom and the 33% $p_{1/2}$ for optimum bonding.

On the basis of simplified calculations assuming the full promotion energy to ${}^1/_3(p_{1/2}) + {}^2/_3\,(p_{3/2})$ orbitals, it was estimated[19] that elements 112, 114, and 118 would be relatively stable as atoms and approach "inert gas" (actually inert volatile liquid) characteristics. Also it was suggested[22] that radon fluoride may be an ionic compound (Rn^+F^- or $Rn^{2+}F^-_2$) rather than a covalently bonded structure and that element 118 would show an even stronger tendency in that direction. Refined calculations would change the numerical values, but it is not likely that the qualitative indications would be changed.

Finally, it may be noted that similar problems arise for bonding with relativistic d or f orbitals in relation to their angular properties, but it is not yet clear what the impact is on chemical properties. This matter deserves future study.

Table VIII
Properties of Au_2

state	R_e, Å	D_e, eV	T_e, eV
X 0_g^+, calcd	2.37	2.27	0
exptl[a]	2.47	2.31[b]	0
A 0_g^+, calcd	2.51	0.79	2.61
exptl[a]	2.57	1.00	2.44
B 0_u^+, calcd	2.50	1.38	3.55
exptl[a]	2.51	1.78	3.18

[a] From ref 26. [b] From ref 11.

Relativistic Calculations for Molecules

A full exact relativistic treatment of electronic motion in a molecule is very difficult, and none has been completed for a molecule which includes heavy, many-electron atoms where the effects we have been considering are chemically significant. But approximate calculations of useful accuracy have been made on two different bases. One method[12,23-25] assumes that the core electrons remain unchanged in molecule formation and replaces their detailed influence on valence electrons by effective potentials. This method was used to treat diatomic gold[12] with the results shown in Table VIII, which show that the properties[11,26] of the two excited spectroscopic states which have been observed as well as those of the ground state are obtained with useful accuracy from the relativistic calculations. Comparison with nonrelativistic calculations for the ground state indicates that the relativistic effects strengthen the bond by 1.0 eV and shorten it by 0.3_5 Å. The anomalous trend in dissociation energies in the series Cu_2, Ag_2, Au_2 was stated above; if the bond energy in Au_2 is decreased by 1.0 eV, the anomaly disappears. Thus the anomaly is primarily caused by the relativistic effects.

Another approximation for relativistic molecular calculations is the one-center method of Desclaux and Pyykkö.[20,27] Here *all* electrons are considered, but only in orbitals centered on the heavy atom. The method gives useful results for compounds of a single heavy atom with hydrogen; there are only valence electrons in the vicinity of the protons. These one-center cal-

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(18) J. Drowart and R. E. Honig, *J. Phys. Chem.*, **61**, 980 (1957); S. A., Shchukarev, G. A. Semenov, and I. A. Rat'kovskii, *J. Inorg. Chem. USSR*, **7**, 240 (1962); D. S. Ginter, M. L. Ginter, and K. K. Innes, *J. Phys. Chem.*, **69**, 2480 (1965).

(19) K. S. Pitzer, *J. Chem. Phys.*, **63**, 1032 (1975).

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

(21) Y. S. Lee, to be published.

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Table IX
Molecular Constants for AuH

R_e, calcd nonrel, Å	1.807,[a] 1.747[b]
calcd relativ, Å	1.522,[a] 1.622[b]
exptl, Å	1.524[c]
D_e, calcd relativ, eV	2.66[a]
exptl, eV	3.37[c]

[a] Effective potential method.[24] [b] One-center method.[27] [c] Experimental.[28]

culations can be made relativistically as well as nonrelativistically, 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.[3]

It is interesting to compare the relativistic effects in AuH with those in Au_2. There are effective potential calculations of Hay et al.[24] and one-center calculations of Desclaux and Pyykkö[27] which are given in Table IX together with experimental values.[28] 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_2.

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[5] 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 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.[29] showed that the spectra of the molecules ReF_6 to PtF_6 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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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 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

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