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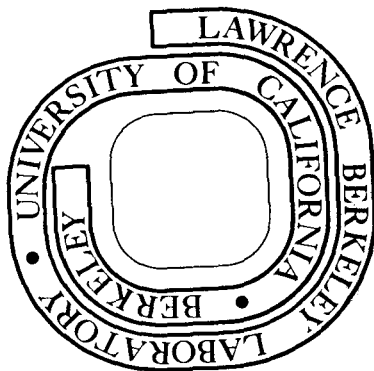
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RELATIVISTIC EFFECTS ON CHEMICAL PROPERTIES

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It was only after a relativistic quantum theory was developed, largely by Dirac, that he made his famous statement¹ in 1929, "...the underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known...". But for most of chemistry one uses nonrelativistic quantum mechanics supplemented by the qualitative rules related to the spin quantum number and the Pauli exclusion principle. These last requirements are an integral part of relativistic quantum mechanics. But an appropriate expansion of the Dirac equation² yields a set of larger terms which comprise the Schrödinger equation together with additional terms whose contribution to the energy is small unless particle velocities approach the velocity of light. Thus, for many chemical problems it is adequate and convenient to solve the nonrelativistic, Schrödinger equation, subject to spin and symmetry or antisymmetry requirements; and then to add the contributions of the smaller terms as perturbations if they are not completely negligible.

The unique but not always the most important of these smaller terms is that for the spin-orbit interaction. For light elements it yields small but readily observed splittings of spectroscopic lines, etc. The magnitude of this spin-orbit term increases rapidly for heavy elements as shown in Table 1.

It is the purpose of this paper to consider the effects on properties of general chemical interest arising from the difference between a fully relativistic treatment and the conventional treatment with the nonrelativistic Schrödinger equation and the appended rules for spin, etc. Since the difference in energy for the two approaches is of the magnitude of the spin-orbit term, we may use the latter as an indicator of the region

Table 1. Energy Terms for Fourth Group Elements in Electron Volts.

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

of interest. A chemical bond energy for relatively large atoms is roughly two electron volts (46 kcal or 190 kJ). From Table 1 we see that the spin-orbit term for a valence electron is small compared to a chemical bond energy for fourth-group elements through tin but becomes larger than the bond energy for lead. Thus we may expect relativistic effects to become important for chemical bonding in the last full row in the periodic table. Let us seek possible anomalies in behavior for the lanthanides and for the all of the heavier elements.

Cotton and Wilkinson,³ 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} , 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.

It is not our primary purpose to present the mathematical formulation or methods of calculation for relativistic quantum mechanics. A brief summary of the equations, orbitals, etc., is given in an Appendix. Also we consider first the conclusions which can be drawn from comparisons of relativistic and nonrelativistic calculations for atoms. There are complete tables of self-consistent-field calculations⁴⁻⁶ yielding orbital energies,

radii of the various orbitals, and other properties. Also the orbital energies are approximately related to experimental ionization potentials.⁷ Thus it is convenient to use this information concerning the atoms to a maximum extent.

Not very many relativistic calculations have been made, as yet, for the electronic motion in molecules. In a second 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.

CONCLUSIONS BASED ON ATOMIC PROPERTIES

In addition to atomic spectral data we have complete tables from Desclaux⁴ based on solution of the Dirac equation and yielding orbital energies, radii, and other properties. Comparable nonrelativistic tables are available from several sources.^{5,6} 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 $j = \ell - \frac{1}{2}$ and $j = \ell + \frac{1}{2}$. 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 fourteen 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 2 gives both the relativistic and nonrelativistic calculated radii for the 5p shell as well as the experimental ionic radii³ for lanthanum and lutecium and for comparison also for yttrium (4p shell). One would not

Table 2. Lanthanide Contraction, 5p Mean Radii (4p for Yttrium) and Observed Ionic Radii, Å.

	nonrel.	calculated <r>			observed ionic radius
		av.rel.	p _{3/2}	p _{1/2}	
Y	.778	.774	.779	.763	.88
La	.970	.958	.971	.931	1.061
Lu	.774	.745	.764	.706	.848

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 0.10₃ Å in all case. The ionic radius of lutecium 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 lutecium. While the relativistic contribution to the total contraction from

La to Lu is only about 10%, it is the relativistic effect which 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 made⁸ for pseudo-atoms 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 3-5. For the radius of

Table 3. Radii $\langle r \rangle$ in Å, Weighted Averages for Relativistic 5d and 6p.

	Pseudo-atom nonrelativ.			Real Atom nonrelativ.			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		.952	1.955		.992	1.734	
Au	.912	2.235		.817	1.958		.839	1.620	
Hg	.849	1.984		.758	1.761		.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

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 4. Calculated Orbital Energies and Experimental Ionization Potentials in eV for Valence Shell Electrons.

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

Table 4 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, 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 pseudo-gold 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,⁹ 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 made¹⁰ for Au_2 and is discussed in the next section.

The electron affinities of these atoms are¹¹ Cu (1.226 eV), Ag (1.303 eV), and Au (2.308₆ 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 semiconductors¹² 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 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 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 3. The contraction of the 6p orbital in thallium is primarily a 4f-shell effect although the relativistic effect is in the same direction. 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 IV through VII, 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 III. 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 5. On a nonrelativistic basis, even with the effect of the 4f shell, all of the energies decrease along

Table 5. The Inert Pair Effect. Orbital Energies for Ge, Sn, and Pb in 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
$\Delta\epsilon$, pseudo-atom	---	---	4.78

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 pseudo-lead, 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.

In various discussions^{13,14} 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 6 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.

Table 6. Valence Orbital Energies in eV and Radii in Å for Uranium.

	Relativ. (wt.av.)	Nonrel.
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

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 data for atoms. Let us now turn to relativistic theory and calculations for molecules for both confirmation of these conclusions and further insight.

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^{10,15-17} 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 gold¹⁰ with the results shown in Table 7, which show that the properties^{9,18} 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 indicate that the relativistic effects strengthen the bond by 1.0 eV and shorten it by 0.35 Å. The anomalous trend in dissociation energies in the series Cu₂, Ag₂, Au₂ was stated above; if the bond energy in Au₂ 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 Pyykko.^{19,20} 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 calculations 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.

Table 7. Properties of Au₂.

State			$R_e(\text{\AA})$	$D_e(\text{eV})$	$T_e(\text{eV})$
X	0_g^+	calc.	2.37	2.27	0
		exp. ^a	2.47	2.31 ^b	0
A	0_g^+	calc.	2.51	0.79	2.61
		exp. ^a	2.57	1.00	2.44
B	0_u^+	calc.	2.50	1.38	3.55
		exp. ^a	2.51	1.78	3.18

^afrom ref.18.

^bfrom ref.9.

Results of one-center calculations¹⁹ for the series CuH, AgH, and AuH are given in Table 8 along with the experimental values.²¹ The effective potential calculations of Hay *et al.*¹⁴ for AuH are also available and the results are included. The relativistic effective-potential value for the interatomic distance agrees well with experiment and a relativistic shortening of 0.285 Å is indicated. The calculated bond-energy value does not agree as well; hence caution is indicated in drawing further conclusions. The results of one-center calculations are evidently very approximate, but they indicate correctly that there is a substantial relativistic shortening and strengthening of the bond in AuH. One concludes from these results, as for those from Cu₂, Ag₂, and Au₂, the anomalous properties of the gold compounds arise primarily because of relativistic effects.

An examination of the angular properties of relativistic orbitals indicates²² that while s orbitals remain good bonding orbitals in the relativistic domain, $p_{1/2}$ and $p_{3/2}$ orbitals are not effective in bonding. It is only by taking the linear combinations $\frac{1}{3}(p_{1/2}) + \frac{2}{3}(p_{3/2})$ which yield essentially the nonrelativistic orbitals that good bonding properties are obtained. When spin-orbit energies are large, this implies further promotion energy to yield an effective valence state. Rough calculations based on this promotion energy have been presented²² in connection with estimates of properties of super heavy elements in the range 112-118. Also the peculiar properties of radon fluoride are considered on this basis.²³ It is found that the promotion energy from the lowest state $^2p_{3/2}$ of Rn^+ to a valence state $\frac{1}{3}(p_{1/2}) + \frac{2}{3}(p_{3/2})$ is so great that an ionic compound Rn^+F^- (or $Rn^{++}F_2^-$) may be more stable than a covalently bonded structure analogous to XeF₂. For element 118 this effect would be even more pronounced.

Table 8. Molecular Constants for CuH, AgH, and AuH.

	CuH	AgH	AuH
R_e , calc.nonrel.(Å)	1.514 ^a	1.692 ^a	1.744 ^a , 1.807 ^b
calc.rel.(Å)	1.501 ^a	1.658 ^a	1.659 ^a , 1.522 ^b
exp.(Å)	1.463 ^c	1.618 ^c	1.524 ^c
D_e , exp.(eV)	2.85 ^c	2.51 ^c	3.37 ^c
calc.rel.(eV)	---	---	2.66 ^b
ΔD_e , (rel.-nonrel.)(eV)	0.05 ^a	0.35 ^a	1.44 ^a , 0.66 ^b

^aRef.19.

^bRef.16.

^cRef.21.

These calculations assuming full promotion to a bonding valence state are at best a crude approximation; the true state will be a compromise with only partial promotion. This is illustrated by recent results for one-center calculations on TlH. Desclaux and Pyykko²⁰ considered the series from BH through TlH. For the molecules where spin-orbit energies are small, the bonding orbital is $\frac{1}{3}(p_{y_2}) + \frac{2}{3}(p_{3/2})$ as is expected. But for TlH it is 61% (p_{y_2}) and only 39% ($p_{3/2}$) and the effect of relativity is to weaken the bond in TlH. These calculations indicate that the relativistic effects strengthen the bond in InH by about 0.3 eV whereas they weaken the bond in TlH by at least 0.5 eV. Thus the qualitative conclusion that relativistic $p_{3/2}$ orbitals are relatively ineffective for bonding is clearly confirmed. But more detailed calculations are needed for various cases to obtain a quantitative measure of this effect.

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 Wilkinson³ 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.*²⁴ 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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APPENDIX

The many-electron relativistic Hamiltonian may be written^{2,4,25} as

$$H = \sum_i H_D(i) + \frac{1}{2} \sum_{i,j} \left[\frac{1}{r_{ij}} + H_B(i,j) \right] \quad (A-1)$$

where H_D is the Dirac one-electron Hamiltonian including the electrostatic attraction of the nucleus, the $1/r_{ij}$ is the interelectronic repulsion, and H_B is the so-called Breit interaction which is small and is commonly introduced only as a first-order perturbation for the total energy.

$$H_D = ic\alpha \cdot \nabla + \beta c^2 - Z/r \quad (A-2)$$

where α and β are fourth-order matrices, as follows

$$\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix} 0 & 0 \\ 0 & -2I \end{bmatrix} \quad (A-3)$$

where, in turn, I is the second-order unit matrix and σ represents the 2x2 Pauli matrices

$$\alpha_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \alpha_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \alpha_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (A-4)$$

In atomic units, which will be used hereafter, $\hbar = m = e = 1$, $c = 137.037$.

This choice of β removes the rest-mass energy.

Relativistic wavefunctions are fourth-order vectors. The first two, "large" components can be thought to correspond to the ordinary Schrödinger wavefunctions for + and - spin, respectively. The third and fourth, "small" components, are purely relativistic and vanish in the nonrelativistic limit $c \rightarrow \infty$. This is demonstrated² by an expansion of equation (A-1) in inverse powers of c , the Pauli approximation. Now the leading terms yield just the nonrelativistic equation. If we treat the next terms as a perturbation and assume spherical symmetry for an atom, their contribution for a given electron is given by the sum of the three following expressions:

$$\epsilon_m = - \frac{1}{2c^2} \int_0^\infty R_{n,\ell}^2(r) [\epsilon_{n,\ell}^o - V(r)]^2 r^2 dr \quad (A-5)$$

$$\epsilon_d = - \frac{1}{4c^2} \int_0^\infty R_{n,\ell}(r) \left[\frac{dV(r)}{dr} \right] \left[\frac{dR_{n,\ell}(r)}{dr} \right] r^2 dr \quad (A-6)$$

$$\epsilon_{so} = - \frac{k+1}{4c^2} \int_0^\infty R_{n,\ell}^2(r) \left[\frac{dV(r)}{dr} \right] r dr \quad (A-7)$$

Here $R(r)$ is the radial factor in the nonrelativistic wavefunction, $V(r)$ the potential energy, $\epsilon_{n,\ell}^o$ the nonrelativistic orbital energy, and $k+1=-\ell$ if $j=\ell+\frac{1}{2}$ or $k+1=\ell+1$ if $j=\ell-\frac{1}{2}$. The first expression is descriptively called the mass-velocity term and yields the effect of increase in mass as the electron velocity approaches c . The second term, called the Darwin term, and the first both shift energies without regard for spin orientation. The third or spin-orbit expression has a coefficient which depends on the product $\vec{\ell} \cdot \vec{s}$ of spin and orbit vectors and is seen to be zero for s orbitals.

The net effect of $\epsilon_m + \epsilon_d$ is to lower the energy for orbitals with appreciable densities near the nucleus; this is most important for s -orbitals as noted above. The spin-orbit term divides orbitals with $\ell \neq 0$ into two categories lowering the energy for $j=\ell-\frac{1}{2}$ and raising the energy for $j=\ell+\frac{1}{2}$. The component of j on the selected axis, m , is a good quantum number but does not affect the energy for an atom, *i.e.* in spherical symmetry.

Powell²⁶ 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 A-1. 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. Also all small components, $f(r)$ are imaginary, *i.e.* contain the factor i .

In the valence shell the small components are relatively unimportant. Hence one can see that s-orbitals and $p_{3/2}$, $m = \pm \frac{3}{2}$ orbitals retain the form given in nonrelativistic treatments with the non-zero large component in the first position for positive spin and in the second position for negative spin. But for $p_{1/2}$ and $p_{3/2}$, $m = \pm \frac{1}{2}$ orbitals, neither large component is zero. In the nonrelativistic limit the $p_{1/2}$ and $p_{3/2}$ energies become equal and the linear combinations which restore the Schrödinger solutions are equally acceptable. But for heavy atoms the $p_{1/2}$ - $p_{3/2}$ energy difference is substantial even in the valence shell.

The chemical bonding properties can be obtained from the angular factors for the large components. The s-orbitals form good sigma bonds and $p_{3/2}$, $m = \pm \frac{3}{2}$ orbitals good pi bonds. But a diatomic molecular orbital of $p_{1/2}$ atomic orbitals is either $\frac{1}{3}$ sigma bonding and $\frac{2}{3}$ pi antibonding, or the reverse; hence, one does not get good bonding from $p_{1/2}$ orbitals.

Table A-1. Dirac Atomic Orbitals. The Angular Factors are Shown Explicitly:
Other Factors are Included in $g(r)$ and $f(r)$ in Each Case.

$$s_{1/2}, m = +\frac{1}{2}$$

$$\begin{bmatrix} g(r) \\ 0 \\ f(r)\cos\theta \\ f(r)\sin\theta e^{i\phi} \end{bmatrix}$$

$$s_{1/2}, m = -\frac{1}{2}$$

$$\begin{bmatrix} 0 \\ g(r) \\ f(r)\sin\theta e^{-i\phi} \\ -f(r)\cos\theta \end{bmatrix}$$

$$p_{1/2}, m = +\frac{1}{2}$$

$$\begin{bmatrix} g(r)\cos\theta \\ g(r)\sin\theta e^{i\phi} \\ f(r) \\ 0 \end{bmatrix}$$

$$p_{1/2}, m = -\frac{1}{2}$$

$$\begin{bmatrix} g(r)\sin\theta e^{-i\phi} \\ -g(r)\cos\theta \\ 0 \\ f(r) \end{bmatrix}$$

$$p_{3/2}, m = +\frac{3}{2}$$

$$\begin{bmatrix} g(r)\sin\theta e^{-i\phi} \\ 0 \\ f(r)\sin\theta\cos\theta e^{i\phi} \\ f(r)\sin^2\theta e^{2i\phi} \end{bmatrix}$$

$$p_{3/2}, m = -\frac{3}{2}$$

$$\begin{bmatrix} 0 \\ g(r)\sin\theta e^{-i\phi} \\ f(r)\sin^2\theta e^{-2i\phi} \\ -f(r)\sin\theta\cos\theta e^{-i\phi} \end{bmatrix}$$

$$p_{3/2}, m = +\frac{1}{2}$$

$$\begin{bmatrix} 2g(r)\cos\theta \\ -g(r)\sin\theta e^{i\phi} \\ f(r)(\cos^2\theta - \frac{1}{3}) \\ f(r)\sin\theta\cos\theta e^{i\phi} \end{bmatrix}$$

$$p_{3/2}, m = -\frac{1}{2}$$

$$\begin{bmatrix} g(r)\sin\theta e^{-i\phi} \\ 2g(r)\cos\theta \\ f(r)\sin\theta\cos\theta e^{-i\phi} \\ -f(r)(\cos^2\theta - \frac{1}{3}) \end{bmatrix}$$

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