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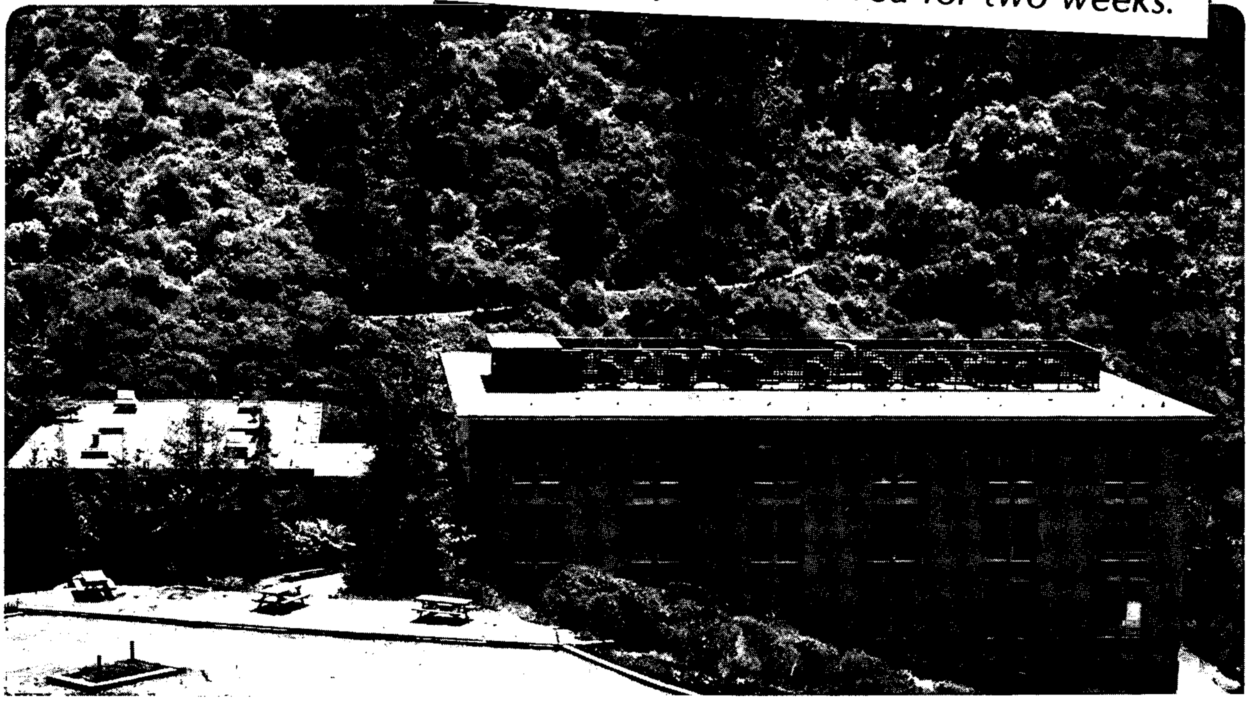

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Relativistic Effects in Chemical Systems

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INTRODUCTION

While the velocity of light c is finite in the real world, most calculations of theoretical chemistry make the approximation $c = \infty$. This is usually a satisfactory approximation for systems of light atoms H, C, N, O, etc., and for most properties of chemical interest. Where heavy elements are involved, however, the nonrelativistic ($c = \infty$) approximation is not adequate. This review concerns the area where relativistic equations must be used for accurate calculations of properties of chemical interest. Only in the last decade have a large and diverse array of relativistic quantum chemical calculations been made.

We define relativistic effects as the differences between calculations for the correct value of the velocity of light and the results for $c = \infty$. To obtain correct results even for $c = \infty$ one must either use the Dirac equation, which yields electron spin, or supplement the Schrödinger equation with an ad hoc assumption about spin. Both of these procedures yield the same results and are commonly termed "nonrelativistic" even though spin is, in a strict sense, a purely relativistic effect.

Indeed, for almost all purposes it is preferable to use the Schrödinger equation with the ad hoc assumption about electron spin. This is simpler mathematically; also it avoids the problem of negative energy solutions of the Dirac equation, which persists even for $c = \infty$. As we shall see below, this difficulty of contamination of the physically significant Dirac states with those related to the negative energy solutions is very troublesome in all-electron molecular problems. Fortunately, this difficulty is avoided in numerical solutions for atoms and in the effective potential methods that are widely used for molecules.

There are a number of anomalous effects in the properties of very heavy elements in relation to the regularities of the periodic table. The two sources of these anomalies are (i) relativistic effects and (ii) the appearance of f-electrons. In the first part of this review these anomalies will be discussed in relation to both of these effects on a qualitative or semiquantitative basis.

The second section presents theoretical methods for quantitative relativistic quantum calculations for molecules, after which the final section presents a selection of the most interesting quantitative treatments of particular molecules.

Previous reviews in English of relativistic quantum chemistry include one by Pyykko (1) which includes methods of calculation as well as results available prior to 1978, and a simultaneously published pair of reviews by Pyykko & Desclaux (2) and by Pitzer (3) which emphasize properties of general chemical interest. A 1982 symposium on Relativistic Effects in Quantum Chemistry (4) included several papers of broad interest. The volume (5) based on the 1981 Advanced Study Institute on Relativistic Effects in Atoms, Molecules, and Solids also contains chapters of chemical interest as well as pertinent underlying theory. The predictions of the chemistry of superheavy elements (above 103) were reviewed by Fricke (6). There are also reviews in French (7,8) and Finnish (9).

RELATIVISTIC EFFECTS AND THE PERIODIC TABLE

Probably the most familiar relativistic effect is the increase in particle mass as the velocity approaches the speed of light. It is the s electrons with no angular momentum that can approach an atomic nucleus most closely and therefore gain the highest velocity. For elements of large atomic number this velocity approaches that of light at a considerable distance from the nucleus. In other words, the mass-velocity effect is substantial for a considerable portion of the s-electron motion. The result is that s orbitals are more concentrated near the nucleus than would be expected nonrelativistically, have contracted mean radii, and have increased ionization potentials. Since outer s orbitals must be orthogonal to all inner orbitals, this contraction in size and increase of ionization energy applies also to valence-level s electrons.

For p electrons the mass-velocity effect is similar to that for s electrons but is much smaller. Now, however, there is also the spin-orbit effect which divides the six p-shell spinorbitals into two $p_{1/2}$ spinors and four $p_{3/2}$ spinors. This spin-orbit effect, which is given by the Dirac equation, is purely a quantum-relativistic effect. The net result of the mass-velocity and the spin-orbit effects for atoms is that the two effects nearly cancel for $p_{3/2}$ electrons but they reinforce for $p_{1/2}$ electrons and yield contractions and energy stabilizations about equal to those of s electrons of the the same principal quantum number.

The direct mass-velocity effect is small for electrons with large angular momentum, but the contraction of inner s and $p_{1/2}$ shells increases the shielding of the nuclear charge. Hence there is generally an expansion and energy destabilization of d and f orbitals. The spin-orbit effect remains substantial with the lower j value ($j=\ell-1/2$) yielding a smaller mean radius and larger ionization energy than the larger j value ($j=\ell+1/2$).

Inorganic chemistry texts commonly list two general effects that appear in the sixth row of the periodic table: the lanthanide contraction and a great enhancement of the inert pair effect. In addition there are several additional anomalies when the properties of a sixth- or seventh-row element are compared to lighter elements of the same group. We now discuss these anomalus effects primarily in terms of the qualitative concepts stated above and the quantitative comparison of Dirac-Fock (DF) calculations of atomic properties with the corresponding nonrelativistic Hartree-Fock (HF) calculations. Desclaux (10) has presented a complete table of DF atomic properties and of the ratios of DF to HF properties.

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 nuclear charge by the 4f electron shell. Thus there is a larger effective core charge for the sixth-row elements and this contracts the outer s, p, and d orbitals.

The contraction for the lanthanides is primarily the 4f shell effect, as supposed. But a comparison (3) of DF and HF results yields a relativistic effect which for Lu is 0.03 A in comparison with a total contraction from La of 0.11 Å. Thus the relativistic effect is not negligible and adds to the 4f shell effect for Lu.

In order to distinguish 4f shell and relativistic effects for the succeeding elements, HF calculations were made (11) for pseudo-atoms in which the nuclear charge was reduced by the number of 4f electrons and the 4f orbitals were deleted. Energies were considered as well as radii. It was found that the relativistic effect becomes more important for these succeeding elements(3,11). Table 1 shows the calculated orbital energies and the experimental ionization potentials for Au and Ag. For the 6s electron in gold the total stabilization of 2.8 eV arises 2/3 from relativistic effects and only 1/3 from the 4f shell effect. One notes also from Table 1 that the relativistic effects are small, but not negligible, for Ag and that both relativistic and 4f shell effects destabilize the 5d electrons in Au. For d-shell effects, which are primarily indirect and may involve cancellations of opposing terms, the situation becomes complex and effects on radii do not necessarily parallel those on energies. Thus the 4f shell effect on the 5d radius for gold is a contraction, but on the energy it is a destabilization.

The appearance, primarily in groups IV through VII, of compounds of 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, 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 2. 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 is bound as strongly in Pb as in Ge and much more so 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 and fifth groups show the same pattern.

There are numerous anomalies in the series Cu, Ag, Au, most of which are related to the contraction and stabilization of the 6s orbital in gold. In addition to the ionization potentials (Table 1), the electron affinities show the anomalous sequence Cu 1.226 eV, Ag 1.202 eV, Au 2.309 eV. The high value for gold is most striking and relates to the unusual compounds CsAu and RbAu which are nonmetallic semiconductors with the salt-like 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.

The dissociation energies of the diatomic molecules are also anomalous: Cu_2(1.95 eV) Ag_2(1.65 eV), Au_2(2.29 eV). Calculations discussed below indicate that the relativistic effect for Au_2 is about 1.0 eV (12). This arises from the contraction and stabilization of the bonding 6s orbitals. The color of gold, in contrast to silver, has been related (2) to the 5d-to-Fermi-level excitation energy which is relativistically reduced in gold as compared to silver.

For mercury one first notes that the anomalous volatility of the element is just the inert pair effect discussed above. The remarkable $Hg_2{}^{+2}$ ion is isoelectronic with Au_2 and presumably has a relativistic stabilization of about 1.0 eV, without which it would never exist as a common aqueous ion.

For thallium and the following elements these effects continue but the large spin-orbit splitting of the energies of the $p_{1/2}$ and $p_{3/2}$ electrons represents an additional relativistic effect. For chemical bonding it is important to know the angular properties of the $p_{1/2}$ and $p_{3/2}$ spinors which are given in detail in a later section. Here we note merely that a $p_{1/2}$ spinor has both σ and π components with respect to bonding along a given axis. Thus, for bonding in $T\ell_2$ a gerade conbination of $p_{1/2}$ spinors yields a molecular spinor which is 1/3 σ_g and 2/3 π_g or 1/3 sigma bonding and 2/3 pi antibonding. The corresponding ungerade molecular spinor is 1/3 sigma antibonding and 2/3 pi bonding. Hence, two thallium atoms in their ground $^2P_{1/2}$ state will not form a strong bond. This effect is discussed further in the last section in relation to Pb_2 and $T\ell H$, as well as to $T\ell_2$.

From the very large spin-orbit effect in Rn^+ it has been speculated (13) that radon fluoride may be an ionic compound, Rn^+F^- rather than following the covalent bonding pattern of the xenon fluorides.

Relativistic effects are presumably very important for the still heavier elements of the actinide series, but there have been few nonrelativistic calculations from which, by difference, the relativistic effects can be obtained. Even approximate, Huckel-type calculations are ordinarily based on parameters chosen from experimental spectra or from Dirac-Fock atomic calculations and, hence, are on a relativistic basis. Lohr & Pyykko (14) developed a relativistic extended Huckel method which has been applied to a number of molecules and ions (15,16).

There are many differences between the properties of the first few actinides and those of the corresponding lanthanides. The prevalence of oxidation states higher than three and as high as six for U, Np and Pu is a fundamental difference which suggests that the

5f electrons are less strongly bound than the 4f electrons in the corresponding lanthanides. This is a relativistic effect. The DF orbital energies for Pu and Sm are 7.5 and 11.3 eV, respectively, but for the 5f orbital energy in a nonrelativistic Pu, the value is 15.8 eV, which is much higher than that for Sm. Hence, there is good reason to expect that nonrelativistic U, Np, and Pu would retain as many unshared f electrons as Nd, Pm, and Sm and as a result would be limited in oxidation number to three.

Thus the existence of uranyl ion UO_2^{+2} as a stable aqueous species is a relativistic effect. The reasons for its linear structure and very short, strong bonds are also interesting, and there are several pertinent calculations (17-25). In 1952 Connick & Hugus (17) argued persuasively for the importance of f-orbital participation in the bonding in UO_2^{+2} and in the analogous NpO_2^{+2} and PuO_2^{+2}. They showed that no other elements with six electrons outside a core formed similar ions and that the only plausible explanation was the involvement of 5f electrons in bonding. The corresponding lanthanide, neodymium, with nonbonding 4f electrons, is very different from uranium as is tungsten where the 4f shell is full and 5f orbitals do not participate in bonding.

The species ThO_2, which is isoelectronic with UO_2^{2+}, has been produced and studied in inert-gas matrices (26). In contrast to the 180° angle in uranyl ion, ThO_2 has a bent geometry (122°). Wadt (24) made relativistic calculations on an equivalent basis for these two species and found agreement with the observed structures. There is a large 5f participation in bonding for UO_2^{2+}, but much less 5f participation in bonding in ThO_2. The back bonding from oxygen in ThO_2 is primarily to 6d orbitals, and Wadt finds that this favors a bent geometry.

Substantial f orbital participation in the bonding is clearly an important aspect of the uranyl ion. There are some other aspects in which Wadt's more fundamental calculations disagree with earlier work by extended by Huckel methods. All of these calculations are relativistic; the differences are in the approximations made, and at present, Wadt's results have the best basis.

The electronic spectra of uranyl compounds have been studied, and various authors have discussed their interpretatation, including very recently Dekock et al (25). There is agreement on most features but some differences remain. Molecular orbitals of symmetries σ_g, σ_u, π_g, π_u are of similar energy and are occupied, but various investigations yield different sequences within this group. The majority population is oxygen 2p for all of these orbitals.

Also very interesting are the cyclooctatetrene sandwich compounds with several actinides. Theory played a major role in the initial discovery of uranocene, $U(C_8H_8)_2$, by Streitwieser & Muller-Westerhoff (27). The key aspect is the availability of 5f orbitals and their participation in bonding. Relativistic effects certainly expand the 5f orbitals and make them more suitable for bonding. There are approximate calculations for several actinocene compounds (28), which were parameterized on a relativistic basis, as well as discussion of the related spectra.

The stable existence of the hexafluorides UF_6, NpF_6, PuF_6 with oxidation number six is a relativistic effect, as discussed earlier, but their octahedral structure is expected. Relativistic calculations of various properties have been reported (29-33).

In the latter part of the actinide series, the f-orbital energies become about equal to those of the corresponding lanthanides, and the chemical properties correspondingly become similar. This equality is for relativistic energies for the f orbitals; nonrelativistic energies would be much higher for the actinides than for the corresponding lanthanides.

As the atomic number increases past 100 the $7p_{1/2}$ orbital becomes much more strongly bound, and Brewer (34) predicted that the ground configuration of Lr would be s^2p rather than s^2d. Desclaux & Fricke (35) have confirmed this result by DF calculations with extensive configuration interaction.

Estimates of the chemistry of post-actinide elements have been reviewed by Fricke (6). Pitzer (36) emphasized the increased tendency toward closed s^2 and $p^2{}_{1/2}$ shells for 112 and 114 which suggests high stability for the atoms. Pyper & Grant (37) have carried out multiconfiguration DF calculations for the 7p atoms, 113-118, and Pyper (38) has discussed the application of these results.

PROCEDURES FOR QUANTITATIVE RELATIVISTIC CALCULATIONS

The driving force behind the procedures here described has been the desire to extend conventional techniques into the heavy atom realm without sacrificing reliability. We must be able to deal not only with large numbers of electrons and the subtleties of electron correlation, but also, because of the large magnitudes of relativistic corrections in heavy elements, with the Dirac formalism. The effective core potential (EP) approximation provides a route by which all three of these difficulties are addressed.

Although accurate all-electron calculations have been carried out within the Dirac-Fock formalism for the heavy atoms (10), to date only one study has been published in which it has been applied in an all-electron ab initio calculation using a multi-center basis to a molecule containing one very heavy atom (39,40). The difficulty of carrying out even the SCF step for AuH demonstrates that such all-electron calculations including CI and two or more heavy atoms will be impractical for some time to come. It also appears that electron correlation, if indeed the concept itself is preserved, generally cannot be neglected.

In contrast to the case of molecules made up solely of light atoms, the inclusion of extensive configuration mixing becomes important for reasons other than those usually attributed to electron correlation. In molecules containing heavy atoms the angular momentum coupling can rarely be approximated accurately as pure j-j or pure L-S, but rather is intermediate between these limiting cases. Thus additional configurations may be required just for the purpose of insuring convergence to a proper electronic state. Clearly, for pragmatic reasons, it is often the case that extensive approximations must be made to make heavy element molecular calculations tractable. Considering the margin for error in even the best light element work, such approximations must be chosen with care to avoid a crucial loss of accuracy.

It is desirable to understand effective potentials on a nonrelativistic basis before considering their derivation in the relativistic domain. Space does not allow a presentation here of the nonrelativistic equations and procedures, but there is an excellent review by Krauss & Stevens (41) in last year's Annual Review of Physical Chemistry. Unless the reader is familiar with effective potentials, this review should be consulted before proceding to the relativistic derivations which follow.

Relativistic Effective Potentials - Formal Aspects

The method detailed here for the inclusion of relativistic effects in molecular electronic structure calculations is grounded in the Dirac-Fock approximation for atomic wavefunctions (42). The premise is that the major effects of the Dirac hamiltonian are manifested in the core electrons and that these effects propagate to the valence electrons. In addition, there are direct effects on the valence electrons arising from their penetration into the core region. Insofar as this is true, the valence electrons can be treated using a nonrelativitic hamiltonian to which is added an operator, the relativistic effective core potential (REP). The REP formally, and internally consistently, incorporates relativistic effects on valence electrons that penetrate the core region and those due to interactions of valence electrons with core electrons. The justification for this premise and the derivation of the precise form of the REP's are given in this section.

We apply the formalism developed nonrelativistically by Kahn et al (43) in a parallel fashion beginning with the Dirac Hamiltonian

$$H^{rel} = \sum_{i} h_D(i) + \sum_{i>j} r_{ij}^{-1} \quad , \tag{1}$$

where h_D is the one-electron Dirac hamiltonian and i and j index the electrons. Many electron relativistic effects, which may be approximated by the Breit interaction terms (42) are omitted. (In all methods developed to date, such effects are included in the form of a first-order correction to the wavefunction due to H^{rel} as defined above.) The eigenfunctions of h_D are four-component Dirac spinors

$$\psi_{nkm}(r,\theta,\phi) = r^{-1} \begin{bmatrix} P_{nk}(r)\chi_{km}(\theta,\phi) \\ iQ_{nk}(r)\chi_{-km}(\theta,\phi) \end{bmatrix} \quad , \tag{2}$$

where the relativistic quantum number $k=\pm(j+{}^1/_2)$ as $j=\ell\mp{}^1/_2$, j is the total angular momentum quantum number, and ℓ is the orbital angular momentum quantum number. The angular factors are defined by

$$\chi_{\gamma m}(\theta,\phi) = \sum_{\sigma=\pm{}^1/_2} C(\lambda\,{}^1/_2\,j;m-\sigma,\sigma)Y_\lambda^{m-\sigma}(\theta,\phi)\phi_{{}^1/_2}^{\sigma} \quad . \tag{3}$$

In Eq. (3) $Y_\lambda^{m-\sigma}$ are spherical harmonics, $\phi_{{}^1/_2}^{\sigma}$ are Pauli spinors, and $C(\lambda\,{}^1/_2\,j;m-\sigma,\sigma)$ are Clebsch-Gordan coefficients. The index λ is defined as $\lambda=|\gamma+{}^1/_2|-{}^1/_2$, where γ is either $+k$ or $-k$.

In an analogous fashion to the atomic Hartree-Fock equations, the angular variables can be eliminated using the Wigner-Eckart theorem in the Dirac equation to yield a set of coupled differential equations depending on r (42).

To construct the Dirac-Fock equations it is assumed that the wavefunctions for an atom having N electrons may be expressed as an antisymmetrized product of four-component Dirac spinors of the form shown in Eq. (2). For cases where a single antisymmetrized product is an eigenfunction of the total angular momentum operator J^2, the N-electron atomic wavefunction may be written

$$\Psi^R = A\,[(\psi_1^c\psi_2^c\cdots\psi_m^c)(\psi_1^v\psi_2^v\cdots\psi_n^v)] \quad . \tag{4}$$

The first product in brackets refers to m core electrons and the second to n valence electrons. A is the antisymmetrization and normalization operator. The total energy is then given by

$$E_T{}^R = \langle \psi^R | H^{rel} | \psi^R \rangle = E_c{}^R + E_v{}^R + E_{cv}{}^R \quad , \tag{5}$$

which is separable into contributions due to core, valence and core-valence interaction energies. Following procedures used for the nonrelativistic case (43), one may combine the last two terms using a modified hamiltonian and the wavefunction corresponding to the valence electrons

$$E_v + E_{cv} = \langle \psi_v{}^R | H_v{}^{rel} | \psi_v{}^R \rangle \quad , \tag{6}$$

where

$$H_v{}^{rel} = \sum_v \{ h_D(v) + \sum_c \; [J_c(v) - K_c(v)] \} + \sum_{v>v'} r_{vv'}{}^{-1} \tag{7}$$

in which $J_c(v)$ and $K_c(v)$ are coulomb and exchange operators. $H_v{}^{rel}$ includes the original Dirac one-electron hamiltonian for the valence electrons plus additional terms that represent the electrostatic effect of the core on the valence orbitals.

The shape-consistent algorithm of Christiansen et al (44) is employed to define nodeless pseudospinors. The wave equation for one valence electron may be written

$$(h_D + U^{core})\ \chi_v^R = \varepsilon_v\ \chi_v^R \quad , \tag{8}$$

where the U^{core} is the REP in the form of a 4 x 4 matrix that operates on the four-component pseudospinors χ_v^R.

The REP U^{core} may be expanded in the angular factors of Eq. (2) and used to construct the Dirac-Fock equations in terms of the radial pseudowavefunction (45)

$$\frac{d}{dr}\begin{bmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{bmatrix} = \begin{bmatrix} -k_v/r & 2/\alpha+\alpha[\varepsilon_v-U_v^Q(r)] \\ -\alpha[\varepsilon_v-U_v^P(r)] & k_v/r \end{bmatrix}\begin{bmatrix} P_v^{ps}(r) \\ Q_v^{ps}(r) \end{bmatrix} \tag{9}$$

The REP's $U_v^P(r)$ and $U_v^Q(r)$ may in principle be extracted using any pseudowavefunction having components P_v^{ps} and Q_v^{ps}. Such REP's would exhibit discontinuities at points corresponding to nodes in P_v^{ps}. This particular problem is removed if nodeless pseudospinors are used. However, nodes cannot be rigorously removed simultaneously from the large and small components. [A procedure for circumventing this difficulty in the context of the Phillips-Kleinman formalism has been proposed by Ishikawa and Malli (46).] The procedure presented here is based on strong evidence that the effect of small components in the valence regions of atoms can be assumed to be negligible (45). The appropriate one-electron radial equation is then

$$[h_v(r) + U_v^{REP}(r)]\ P_v^{ps} = \varepsilon_v\ P_v^{ps}(r) \quad . \tag{10}$$

where h_v is the nonrelativistic Schrodinger hamiltonian for the valence electron.

Atoms having more than one valence electron are treated in a parallel fashion using two-component pseudospinors and the many electron analog of Eq. (8) to yield

$$U_{\ell j}^{REP} = (^1/_2\ \nabla^2 + Z/r - W_k + \varepsilon_{\ell j})\ \chi_{\ell j}\ /\ \chi_{\ell j} \quad . \qquad (11)$$

In Eq. (11) W_k represents the two-electron integrals involving pseudospinors χ_k and all remaining pseudospinors.

It is clear from Eq. (11) that a different REP arises for each pseudospinor. The complete REP is conveniently expressed in terms of products of radial functions and angular momentum projection operators, as has been done for the nonrelativistic Hartree-Fock case (43). Atomic orbitals having different total angular momentum j but the same orbital angular momentum ℓ are nondegenerate in j-j coupling. Therefore the REP is expressed as

$$U^{REP} = \sum_{\ell=0}^{\infty} \sum_{j=|\ell-^1/_2|}^{|\ell+^1/_2|} \sum_{m=-j}^{j} U_{\ell j}^{REP}(r)\ |\ell jm\rangle\langle \ell jm| \quad . \qquad (12)$$

The projection operator $|\ell jm\rangle\langle \ell jm|$ is comprised of the two-component angular functions of Eq. (2) that are eigenfunctions of the Dirac hamiltonian.

In theory an infinite number of calculations for highly excited states is required to complete the expansion of the EP given by Eq. (11), since there are only a few occupied valence orbitals in neutral atoms. This difficulty also exists in the nonrelativistic case and is resolved by using the closure property of the projection operator with the assumption that radial parts of EP's are the same for all orbitals having higher angular quantum numbers than are present in the core. The same approximation is applicable in our approach if relativistic effects are not too different for electrons in the highly excited orbitals. We expect that this is true since those electrons spend less time near the nucleus. Then the REP may be given by

$$U^{REP} = U_{LJ}^{REP}(r) + \sum_{\ell=0}^{L-1} \sum_{|\ell-1/2|}^{\ell+1/2} \sum_{m=-j}^{j} \left[U_{\ell j}^{REP}(r) - U_{LJ}^{REP}(r)\right] |\ell j m\rangle\langle \ell j m| \ . \qquad (13)$$

A weighted average REP (AREP) is defined as follows (45)

$$U^{AREP} = U_{L}^{AREP} + \sum_{\ell=0}^{L-1} \sum_{m=-\ell}^{\ell} \left[U_{\ell}^{AREP}(r) - U_{L}^{AREP}(r)\right] |\ell m\rangle\langle \ell m| \ , \qquad (14)$$

where

$$U_{\ell}^{AREP} = (2\ell+1)^{-1}\left[\ell U_{\ell,\ell-1/2}^{REP} + (\ell+1) U_{\ell,\ell+1/2}^{REP}(r)\right] \ . \qquad (15)$$

The AREP has the advantage that it may be used in standard molecular calculations that are based on Λ-S coupling (47). The AREP may be interpreted as containing the relativistic effects included in the Dirac hamiltonian with the exception of spin-orbit coupling. This form is the same as that presented by Kahn et al (48) which is based on the relativistic treatment of Cowan and Griffin (49). The hamiltonian employed by Cowan and Griffin is essentially the Pauli approximation to the Dirac hamiltonian with the ad hoc omission of the spin-orbit term.

Definitions of the AREP and REP, Eqs. (14) and (13), can be combined to reveal a useful form for the spin-orbit operator (50,51),

$$H^{SO} = \sum_{\ell=1}^{L} \Delta U_{\ell}^{REP}(r)\Big[\ (\ell/(2\ell+1)) \sum_{m=-\ell-{}^1/_2}^{\ell+{}^1/_2} |\ell,\ell+{}^1/_2,m\rangle\langle\ell,\ell+{}^1/_2,m|$$

$$-\ ((\ell+1)/(2\ell+1)) \sum_{m=-\ell+{}^1/_2}^{\ell-{}^1/_2} |\ell,\ell-{}^1/_2,m\rangle\langle\ell,\ell-{}^1/_2,m|\ \Big] \quad , \qquad (16)$$

where

$$\Delta U_{\ell}^{REP}(r) = U_{\ell,\ell+{}^1/_2}^{REP}(r) - U_{\ell,\ell-{}^1/_2}^{REP}(r) \quad . \qquad (17)$$

This form of H^{SO} has been used with considerable success in applications to molecules containing only light atoms (52) as well as to heavy atom molecules (53).

An alternative equivalent form of H^{SO} has been proposed (54) that is more appropriate for use with a standard polyatomic integrals program that computes angular and radial integrals (55). It is derived by transforming the projection operators $|\ell jm\rangle\langle\ell jm|$ to a form involving only projection operators $|\ell m\rangle\langle\ell m|$ and spin operators

$\underset{\sim}{S}$ and orbital angular momentum operators $\underset{\sim}{\ell}$. The spin-orbit operator then becomes (54)

$$H^{SO} = \underset{\sim}{S} \cdot \sum_{\ell=1}^{L} \left(2/(2\ell+1)\right) \Delta U_{\ell}^{REP}(r) \sum_{m=-\ell}^{\ell} |\ell m\rangle\langle \ell m|\underset{\sim}{\ell}|\ell m\rangle\langle \ell m| \quad . \qquad (18)$$

The $U_{\ell j}^{REP}(r)$, $U_{\ell}^{AREP}(r)$, and terms $\Delta U_{\ell}^{REP}(r)$ in H^{SO} of Eqs. (11), (15) and (17) or Eq. (18), respectively, are derived in the form of numerical functions consistent with the large components of Dirac spinors as calculated using the Dirac-Fock program of Desclaux (56). These operators have been used in their numerical form in applications to diatomic systems where basis sets of Slater-type functions are employed (12,53,57,58). It is often more convenient to represent the EP's as expansions in exponential or Gaussian functions (43,45,47). The general form of an expansion involving M terms is

$$U_{\ell}^{AREP}(r) = r^{-2} \sum_{i=1}^{M} C_{\ell i}\, r^{n_{\ell i}} \exp(-\alpha_{\ell i} r^{x}) \quad , \qquad (19)$$

where x=1 for exponential and x=2 for Gaussian functions and the $n_{\ell i}$ are integers. Similar expansions may be used to represent $U_{\ell j}^{REP}(r)$ and $\Delta U_{\ell}^{REP}(r)$. The numerical forms of these operators are fitted using a nonlinear least squares technique thereby yielding optimum values of the $C_{\ell i}$ and $\alpha_{\ell i}$.

In applications to atoms and molecules the REP's in the form of Eq. (12) or the AREP's in the form of Eq. (14) are used in the valence hamiltonian

$$H = \sum_{\mu=1}^{n_v} \left[-{}^1/_2 \, \nabla_\mu^2 + \sum_\alpha \left(-Z_\alpha / r_{\alpha\mu} + U_\alpha^{EP} \right) \right] + \sum_{\mu>\nu}^{n_v} r_{\mu\nu}^{-1} \quad , \qquad (20)$$

where n_v is the number of valence electrons, and U_α^{EP} refers to a relativistic, an averaged relativistic, or a nonrelativistic effective potential that represents the core electrons of atom α. If the U_α^{EP} are nonrelativistic or averaged relativistic EP's, the wavefunction for the n_v-electron system may be represented by linear combinations of spinorbitals, and standard electronic codes may be employed for their calculation. The only alteration in the procedure for using such codes is the necessity to incorporate an additional set of one-electron integrals involving the basis functions and the EP (43,45).

An interesting application of the AREP technique involves the computation of atomic dipole polarizabilities for Rb and Cs, for which spin-orbit effects should be negligible. Although the alkali metals could be treated as one-valence-electron atoms using EP's, previous work has shown that important correlation effects arise due to the next inner electron shell. Thus Rb and Cs were treated as nine electron atoms (59). The REP's, however, were generated from atomic positive ion wave functions to avoid complications due to the presence of two valence shells of the same angular symmetry [see Refs. (43) and (45)]. A basis set of STF's, including diffuse functions, was generated, and coupled-Hartree-Fock calculations were carried out to determine the polarizabilities. However, as in the case of the light alkali metals, a CI procedure consisting of single and double promotions was required. Polarizabilities can be particularly difficult to compute and the excellent agreement between the computed and experimental values demonstrates quite clearly the reliability of the shape-consistent EP technique for this property.

If the REP's of Eq. (12) are used, the presence of the projection operators $|\ell jm\rangle\langle\ell jm|$ dictates that the valence wavefunctions must be comprised of two-component atomic spinors (TCAS) involving the P_{nk} of Eq. (2) (58). Whereas the incorporation of a nonrelativistic EP requires only the computation of a new set of one-electron integrals, the use of U^{REP} and TCAS requires the computation of all one- and two-electron integrals. Malli and Oreg (60) have derived the relationship between diatomic molecular integrals in a basis set of four-component Dirac spinors [Eq. (2)] and spinorbitals that are products of complex Slater-type functions (STF) and α and β spin functions. These relationships involve integrals with respect to the STF's and factors that include the proper Clebsch-Gordan coefficients that render the resulting wavefunction an eigenfunction of the total angular momentum operator. This ω-ω coupling procedure has been specialized to the case of basis sets of TCAS for closed and open shell SCF (58) and MCSCF (61) calculations on linear molecules.

The symmetry properties of diatomic molecules in the double group representation may be found in the work by Malli & Oreg (60). However, the molecular spinors which are eigenfunctions of the REP of Eq. (12) have only two components while the Dirac spinors have four components. In linear molecules, the angular symmetry of a state of a molecule is defined by the total electronic angular momentum Ω, as in Hund's case c (62), and that of i'th molecular orbitals by $m_i = \pm\omega_i$. The two orbitals with $m_i = +\omega_i$ and $m_i = -\omega_i$ are degenerate and constitute a shell. Because spin is incorporated in the orbital, each molecular orbital can accommodate only one electron. With these characteristics, one can derive the SCF theory for the two-component molecular spinors (TCMS) for diatomic molecules by following the procedures that have been formulated for conventional nonrelativistic molecular calculations (63).

When the variational procedure is applied to the energy expression, one obtains equations that are essentially the same as the nonrelativistic equations [Eqs. (12)-(16) of Ref. (63)]. The open-shell configurations which can be treated with the formalism of Ref. (58) are limited to the cases where each open shell belongs to a different symmetry. This formalism may be easily extended to simple multi- configuration SCF calculations using standard nonrelativistic computer codes such as the Bison MCSCF programs (64).

Unfortunately, due to the fact that the angular momentum coupling is just as unlikely to be pure j-j as L-S, single configuration or even small MCSCF calculations are not appropriate in many cases for molecules containing atoms from the lower portion of the periodic table. For the heavier elements the coupling is often intermediate between the two extremes. To deal effectively with these intermediate coupling cases at the SCF level would require MCSCF calculations that incorporate large numbers of configurations. To date such calculations have not been done.

Although the intermediate coupling problem has not received much attention at the SCF level, several methods have been developed in which the spin-orbit coupling is introduced into a normal L-S coupling calculation in a final configuration interaction step. One procedure employed (53,65-68) has been to carry out normal L-S coupling SCF calculations using the AREP's of Eq. (14) to form the molecular orbital basis set used as a starting point for CI calculations. The usual AO to MO integral transformation is carried out and the CI matrix formed. However, instead of the relatively simple L-S coupling configuration list, the configuration expansion is augmented to cover the entire intermediate coupling range. In the simplest cases this is achieved by selecting a set of reference configurations which spans the coupling range for the important valence electrons (53) (typically ten to twenty terms have been used). Additional configurations are generated by promoting electrons from the reference configurations using the usual L-S coupling electron correlation conventions. In more complicated cases it may be necessary to carry out numerous trial calculations or a limited full-valence CI calculation (67) (in the intermediate coupling regime) to determine the important reference configurations.

Since the final configuration lists may be an order of magnitude or more longer than those required for equivalent light element work, configuration selection techniques have been extensively employed

(67). The CI matrix is generated in the usual manner except that now the full REP (AREP plus spin-orbit operator) is included in the molecular hamiltonian. A complication of this approach is that some matrix elements that arise due to the spin-orbit operator are complex when computed in terms of the usual cartesian basis sets generally employed in L-S coupling calculations. That is, the CI matrix is hermitian but complex, and the standard diagonalization programs cannot be used. However, in the REP formalism, there are few imaginary or complex elements to deal with. Furthermore iterative diagonalization procedures, such as that developed by Davidson (69), are very easily modified to take such problems into account with relatively little loss in speed.

It is, of course, also possible to carry out CI calculations in two stages with the electron correlation terms in the first stage for each L-S configuration and then the spin-orbit effects in a second stage. This has been done with semi-empirical spin-orbit operators in several investigations (32,70). From the current viewpoint, however, there seems to be no advantage to the two-stage method.

Alternate procedures have been proposed for REP's. Space does not allow a detailed discussion of these approaches. Fortunately many of these were discussed by Krauss & Stevens (41) in their chapter in last year's Annual Review of Physical Chemistry. The variant in which the AREP's are calculated directly (48) from a spin-suppressed atomic calculation (49) has been discussed above. Also to be noted is the use of REP's in density functional calculations. This was developed by Hamann et al (71) and has been described more fully (72) along with a compilation of EP's for the entire periodic table.

EXAMPLES OF RELATIVISTIC CALCULATIONS FOR MOLECULES

Some of the earliest molecular calculations that included a rigorous treatment of relativistic effects were done by Desclaux & Pyykko using the one-center numerical Dirac-Fock approach (73-79). One-center expansions are not particularly reliable in absolute terms and break down entirely for large internuclear separations. The authors, however, computed both relativistic and nonrelativistic (by adjusting the speed of light) molecular properties and the differences are useful indicators of the magnitudes of the relativistic effects. They studied the hydrides of several groups of the periodic table. These calculations provide an estimate of the relativistic bond length contraction as a function of the column in the periodic table. For boron and carbon they found no significant contraction, but for the column containing Aℓ through Tℓ they computed contractions of approximately, .002, .02, .07, and .2 bohr, respectively. These values correspond rather closely to the relativistic contractions of valence atomic orbitals published by Desclaux (10) and suggest that the two are intimately related. Unfortunately, one-center calculations are incapable of estimating dissociation energies and are inadequate for bond lengths for molecules containing more than a single heavy atom.

Hay et al (80) computed by EP methods the relativistic contractions for AuH to be 0.26 A. This is about three times that from the one-center calculations of Desclaux & Pyykko (74). Hay et al found a relativistic increase of about 0.5 eV in the dissociation energy of AuH.

Recently Lee & McLean (39,40) have published all-electron LCAO-SCF relativistic calculations on AgH and AuH. They reported relativistic bond length contractions of 0.08 and 0.25 A, respectively, and increases in dissociation energies of 0.08 and 0.42 eV. The relativistic contraction of 0.26 A from REP calculations (80) agrees well with this more rigorous value of 0.25 A for AuH. Unfortunately, all-electron calculations involving heavy atoms, even for hydrides, are extremely difficult and to date these are the only calculations of their type.

Some of the earliest relativistic molecular calculations involving more than one heavy atom were done by Lee et al (12) on the ground state of Au_2. Au_2 was chosen because the $5d^{10}6s$ Au valence electron configuration gives rise to primarily s bonding, and relativistic spin-orbit corrections (which greatly complicate other cases) should be negligible for the ground state. More importantly, however, the Au_2 bond is anomalously strong, stronger even than that in Cu_2 and much stronger than that of Ag_2. The relativistic correction to the bond strength was computed to be approximately 1 eV, or twice that for AuH. This gives a "nonrelativistic" bond strength of 1.3 eV (the experimental value is 2.3 eV) as compared to 2.1 and 1.5 eV in Cu_2 and Ag_2, respectively. The anomaly appears to be due almost entirely to relativity. In this work the bond length contraction was computed to be 0.35 A, only slightly larger than the value Hay et al obtained for AuH.

Using the same techniques and effective potentials as above, Ermler et al (57) evaluated several excited state dissociation curves for Au_2. However, for the excited states the 5d participation results in significant spin-orbit corrections, which were included using a semiempirical procedure.

The above Au_2 and Au_2^* calculations employed effective potentials based on the Phillips-Kleinman atomic orbital transformation. It is now well known that such potentials are not particularly reliable for computing molecular properties and typically underestimate bond lengths and overestimate dissociation energies. Furthermore, the relativistic and nonrelativistic potentials employed in this work are not precisely comparable. Very recently Ross & Ermler (81) have repeated ground state calculations on Au_2 using the more reliable shape-consistent potentials. Employing configuration interaction expansions equivalent to Lee et al (12) they obtained a bond length 0.14 A longer. When compared to nonrelativistic all-electron calculations (12) this gave a relativistic bond length contraction of about 0.2 A. They also looked at Ag_2 and in the same manner computed a bond length contraction of 0.05 A. Thus Ross and Ermler obtained homonuclear relativistic contractions of about the same magnitude that Lee and McLean found for the hydrides. Based on the results of these two sets of calculations, it would appear that the model of the relativistic atomic orbital contraction as a shift in the bonding radii is too simple. On the other hand, since we are considering shifts of only a few tenths of Angstroms, we may be expecting too much of the bond radius model.

Ziegler et al (82,83) and Snijders & Pyykko (84) have suggested that the bond length contraction is independent of the orbital contraction but rather it is a "direct" result of the Dirac hamiltonian. They arrived at this conclusion after observing that the contraction could quite reliably be computed from the nonrelativistic molecular wavefunction by replacing the Schrodinger hamiltonian with a relativistic one. The energy then is the "first-order" relativistic energy. Comparisons were made using both the one-center approach of Desclaux and Pyykko and using the Hartree-Fock-Slater (HFS) method. These results were recently verified using the molecular generalization of the Cowan-Griffin atomic procedure (85). In detailed calculations Ziegler et al (83) indicated that the contraction occured as a result of the relativistic stabilization of the electron density build-up near the nuclei, which in turn resulted from the overlap of the valence orbitals on one center with the core on another. The interpretation of these studies has not been universally accepted. First, most comparisons were done using the rather approximate HFS procedure. But more importantly, it is not clear that the molecular buildup of electron density near the nuclei differs altogether from the relativistic AO contraction. Indeed Schwarz and co-workers (86) have argued that the bond length contraction can be obtained in either of two equivalent ways: (i) by the first-order energy method employed by Zeigler et al (nonrelativistic wavefunction and relativistic hamiltonian), or (ii) by replacing the nonrelativistic wavefunction by its relativistic counterpart, which includes the orbital contraction (relativistic wavefunction and nonrelativistic hamiltonian). This interpretation is based on the double perturbation theory "equivalence theorem", using the relativistic correction to the hamiltonian and a shift in the internuclear separation as perturbations.

This anaysis has recently been tested for Au_2 and Xe_2^+ within the effective potential approximation (87). Four sets of calculations were carried out: nonrelativistic, first-order relativistic, fully relativistic, and first-order nonrelativistic (relativistic wavefunction with nonrelativistic hamiltonian). The computed R_e values were, respectively, for Au_2 3.01, 2.67, 2.58, and 3.14 Å and for Xe_2^+ 3.24, 3.18, 3.19, and 3.24 Å. For these cases then, the analysis of Schwarz et al is clearly inappropriate, and it may indeed be the case that the nonrelativistic electronic "contraction" stabilized in first-order calculations is independent of the usual relativistic AO contraction. Nevertheless, since the "contraction" is only stable in the presence of the relativistic hamiltonian, it is still a relativistic orbital contraction, but now at a molecular level.

Clearly, for atoms as heavy as Au the first-order approach to relativistic corrections is inadequate and analyses of the type employed in Refs. (82-85) may not be accurate. The more detailed aspects of relativistic bond length contraction are still somewhat of an open question. First, the precise mechanism by which it occurs has not been determined unequivocally. In addition, the computed magnitudes often vary by as much a factor of two or more from calculation to calculation.

A very interesting problem has to do with the effect of spin-orbit coupling on the formation of chemical bonds. This possibility was first brought up by Pitzer in 1975 (3); however, it is a much more difficult problem to deal with computationally (as compared to the bond contraction) and only recently have accurate calculations for heavy element systems appeared in the literature.

Spin-orbit coupling might also have a non-negligible impact on atomic and molecular polarizabilities, where, in the simplest case, a weak field is applied which disrupts the atomic spherical symmetry. Stevens and Krauss (88) have carried out comparative calculations on several heavy element species that exhibit such effects.

For molecular calculations involving only the lighter elements, or even heavier elements, provided bonding is dominated by s character, spin-orbit effects can probably be added as a final correction to standard, Hund's case a coupling, calculations. The principal difficulty of this approach is in determining the spin-orbit matrix elements. In all-electron calculations they can be determined using the usual Breit-Pauli operator [see Langhoff & Kern (89) for a review of such procedures]. But for effective potential calculations the all-electron operator is no longer appropriate and various semi-empirical and effective operator schemes have been devised (90-92). We note at this point that, although spin-orbit coupling is a relativistic effect, for purposes of limiting the size of this review, it is considered here primarily in the context of the full Dirac Hamiltonian. As such we do not discuss applications to light atom systems where the spin-orbit effect is treated as a perturbation. The article by Langhoff & Kern should be consulted for a discussion of such applications.

If one assumes a very strong spin-orbit effect, then it is appropriate to set up the problem in terms of molecular spinors, Hund's case c, analogous to atomic j-j coupling. The spin-orbit energy is then included at the first stage of the calculation. Lee et al (45) were the first to use this approach in calculations on atomic Xe and Au, and later in molecular calculations on Au_2^+, TℓH, PbSe, and PbS (58). Schwarz and coworkers (51,93) have developed a similar molecular j-j coupling technique but using more approximate effective potential operators. Christiansen & Pitzer extended the technique to do simple j-j coupling MCSCF calculations on TℓH (61), $Tℓ_2$, $Tℓ_2^+$ (94), and Pb_2 (95).

The mechanism by which spin-orbit coupling can impact molecular bonding becomes clearer when the wavefunction is reformulated in terms of molecular spinors.

The $p_{1/2}$ spinors are combinations of sigma-type and pi-type spin orbitals (ignoring the small components) with coefficients of 1/3 and 2/3, respectively. Therefore a molecular spinor formed as a sum or difference of atomic $p_{1/2}$ spinors on two centers will be 1/3 sigma bonding and 2/3 pi antibonding or just the reverse. In either case one would expect only a weak bond to form. On the other hand, the $p_{3/2}$ $(m=\pm^1/_2)$ atomic spinors are 2/3 sigma and 1/3 pi. Because of the difference in the component signs, linear combinations of $p_{1/2}$ and $p_{3/2}$ spinors can be made to obtain pure sigma or pure pi spin-orbitals, and this, of course, occurs for the lighter elements. However, for the heavier elements such as Tℓ, Pb and Bi the energy gap between the 1/2 and 3/2 spinors is approximately one electron volt and the appropriate mixing is not nearly as readily achieved. For this reason one would expect only very weak bonds to form between two Tℓ atoms or between Pb atoms which in their ground atomic states have only $p_{1/2}$ electrons. For Pb the problem is somewhat more complicated in that the two $p_{1/2}$ electrons form a closed subshell. From this point of view, Pb is somewhat comparable to Be. Bismuth, on the other hand, in addition to the closed $p_{1/2}$ subshell has a single $p_{3/2}$ electron. If the $m=\pm^3/_2$ spinors are used a single pi bond is readily formed in Bi_2. This is in contrast to the triple bond of N_2. Similar combinations can of course be made for heteronuclear molecules. For instance TℓBi would be expected to form a single stable bond that is roughly half sigma and half pi. Furthermore one would expect to see some effect, though probably not as dramatic, for bonds between a heavier element and a lighter one, such as in TℓH.

The above discussion presumes that $p_{1/2}$ to $p_{3/2}$ promotion is unlikely due to the large energy difference, and for this reason L-S coupling is no longer appropriate. Unfortunately, in most cases pure j-j coupling is also inappropriate. Perhaps the best example of this is Pb_2 for which simple j-j coupling SCF or even MCSCF calculations suggest little or no bonding, whereas the Pb_2 bond energy is known to be about 0.9 eV. For these heavy elements the coupling is typically intermediate between the two extremes, and in practice the formulation of the wavefunction must be sufficiently flexible to cover the full range for the various electronic states. If the wavefunction is written as a linear expansion (as in configuration interaction calculations), the expansion terms must be chosen with both electron correlation and intermediate angular momentum coupling in mind.

TℓH is one of the simplest molecules for which one would expect to observe substantial angular momentum coupling effects. Dissociation curves for six low-lying states of TℓH were determined by Christiansen et al (53) using L-S coupling SCF calculations followed by a spin-orbit CI as discussed in an earlier section. The lowest two 0_g^+ curves were found to agree with the experimentally determined curves from Ginter & Battino (96), indicating the reliability of this particular computational technique. The inner walls of the computed curves are slightly too repulsive, probably due at least in part to the neglect of d-shell promotions in the CI calculation.

From the discussion of atomic spinors, one would expect the ground state bond to be considerably weaker than it would have been had the spin-orbit coupling been weaker. Indeed, Pitzer & Christiansen (97) have shown in MCSCF calculations that the spin-orbit coupling reduces the bond strength by about 25 percent.

$T\ell_2$ is a more extreme example of the effects of spin-orbit coupling on chemical bonding. Early j-j coupling MCSCF calculations (94) indicated that $T\ell_2$ was only weakly bonded in its lowest energy configuration. From figure 1, it is apparent that the spin-orbit coupling lowers the atomic asymptote well below the L-S coupling bond. The $^3\Pi_u$ state gives rise to the 0_u^- and 1_u states whereas the 0_g^+ comes from $^3\Sigma_g^-$ and $^1\Sigma_g^+$. In addition, these calculations indicated that, although the neutral molecule is only weakly bonded, the $(1/2)_g$ state of the molecular ion has a bond strength of about 0.5 eV, which is consistent with mass spectral data.

More recently, intermediate coupling calculations have been used to determine the spectroscopic properties and dissociation curves for several low-lying states of $T\ell_2$ (65). All three lowest energy states are bound, but only weakly. The lowest 0_g^+ curve shows clearly an avoided crossing of the $^3\Sigma_g^-$ and $^1\Sigma_g^+$ curves shown in figure 1. In contrast to $T\ell H$, the angular momentum coupling for the lowest energy states of Tl_2 is predominantly j-j. The weak bond in the 0_u^- ground state is in apparent conflict with the value given by Balducci & Piacente (98) (0.6±0.15 eV) based on mass spectral data. However, a reinterpretation of the experimental data using the molecular parameters from the four lowest energy states gives a bond of about 0.37 eV (±0.15) which is in marginal agreement with the computed values, assuming a similar error limit for the computation.

Balasubramanian & Pitzer (68) have carried out calculations for several states of Sn_2 and Pb_2 using essentially the same intermediate coupling procedure as above. These calculations provide an interesting comparison, with the spin-orbit splitting increasing from Sn to Pb by about a factor of four.

For Sn_2 the spin-orbit splitting is much smaller than the bond energy. The lowest energy $^3\Sigma_g^-$ state is split with the 0_g^+ component lowest. The three j-j states that arise from $^3\Pi_u$ are only slightly higher in energy. The $^1\Sigma_g^+$ (π_u^4) which is the ground state in C_2 is important only at short interatomic distances where it yields an avoided crossing in the 0_g^+ states.

In Pb_2 the $^1\Sigma_g^+$ and $^3\Sigma_g^-$ states are much closer in energy. As compared to Sn_2, in the presence of the spin-orbit coupling, the $^1\Sigma_g^+$ produces a marked shoulder on the repulsive portion of the ground 0_g^+ curve. The 0_g^+ to 1_g energy gap is considerable, and the u states are one eV or more above the ground state. These calculations for Pb_2 have been comfirmed by subsequent experimental results of Sontag et al (99).

Sn_2 is reasonably well represented in L-S coupling with the spin-orbit effects as a mild perturbation, whereas for Pb_2, spin-orbit coupling reduces the ground state bond strength by a factor of two. However, as stated earlier, simple j-j couping alone is also inadequate. The coupling in Pb_2 is quite intermediate, at least for the low energy states.

The review by Pitzer (100) gives somewhat more detail concerning the molecules Au_2, $T\ell_2$, $T\ell H$, Pb_2, and Sn_2. In addition to the homonuclear diatomics, Balasubramanian & Pitzer (101-104) have carried out comparable calculations for the oxides of Pb and Sn and also for the hydrides, all in intermediate coupling. Wang & Pitzer have studied PtH and PtH^+ bonding, particularly as it relates to chemisorption phenomena (105). Balasubramanian has reported similar calculations for $T\ell F$ (106) and for several positive ions including SnO^+ and PbO^+ (107).

Christiansen (67) has recently completed calculations for the ground state of Bi_2 which is dominated by the $^1\Sigma_g^+$ triple bonding configuration (as in N_2). However, the spin-orbit coupling mixes in considerable $^3\Pi$ character (about 25 percent).

For the Tl, Pb, Bi series of homonuclear diatomics, one can see that as electrons are added to the 6p shell, the impact of spin-orbit coupling decreases. This is what one would expect in terms of the additional electrostatic interactions and, of course, for the completely filled shell, the $p_{1/2}$, $p_{3/2}$ problem should not arise. Another trend that has been observed in intermediate coupling calculations is that for a given molecular state, L-S coupling is generally more important for the equilibrium atomic separation and becomes less important as the interatomic distance is increased.

These ideas were discussed recently by Pyykko (108). Pyykko et al (109) have also evaluated the effects of d orbitals on bond lengths in small molecules containing heavy atoms.

Laskowski and coworkers have employed AREP's in CI calculations on CrI (110) and CsO (111). Krauss & Stevens have utilized an AREP in studies of UO (112) and UH and UF (113) and their ions. Hafner et al (114) have used REP's based on a model potential approach in a study of relativistic effects in Au_2^+, $T\ell_2$, and Pb_2. Pelissier (115) has performed SCF and CI calculations on Cu_2 using an AREP derived from an approximate second-order representation of the Dirac hamiltonian (116). Teichteil and coworkers used a similar formalism (117) in a study of InH and certain excited states of Ar_2 (118). Celestino & Ermler (119) carried out CI calculations on the electronic states arising from the 6s and 6p shells in Hg_2 and $T\ell Hg$ using AREP's and included the effects of spin-orbit coupling in a semi-empirical (90) fashion.

For nonlinear polyatomic molecules different calculational codes must be used (as compared to diatomic molecules) and few results have been reported which are based on the more rigorous procedures. Noell et al (120) have reported SCF calculations on complexes of platinum including $Pt(PH_3)_n$ using REP's based on the Cowan-Griffin hamiltonian (48,49). Hay (121) has investigated the interaction between Pt and ethylene using this type of REP for Pt. Basch & Cohen (122) have published an SCF study of the linear complex PtCO using an AREP on Pt that was based on a formalism whereby the spin-orbit operator was "averaged" out of the numerical DF procedure.

Most notable are the studies of UF_6 and $Re_2Cl_8^{-2}$ by Hay (33,123). The paper on UF_6 also discusses the calculational methods. $Re_2Cl_8^{-2}$ is of special interest because of the apparent quadruple bond with a δ component. The studies of UO_2^{+2} and ThO_2 (24) were discussed briefly in the first section and use similar methods. All of these calculations use semi-empirical spin-orbit operators (91), which are probably a reasonable approximation in these cases where the spin-orbit energies are not too large. Codes for nonlinear molecules using the ab initio spin-orbit operator of Eq. (18) have been developed (54) but results have not yet been published.

There have been a large number of studies of relativistic effects on chemical bonding that employed various semi-empirical approaches. A representative list includes CNDO calculations on $Pt(Cl_6)^{-2}$ (124), an extended Huckel study of the halides BiX_3 (125), relativistic Xα calculations on $PbMo_6S_8$ (126), and Dirac-Fock-Slater calulations on CsH and the halides CsX (127) and on I_2 and HgI_2 (128).

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Table 1 Calculated orbital energies (ε) and experimental ionization potentials (IP) in eV for valence shell electrons

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

Table 2 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
Δε, relativ	8.23	7.17	8.93
Δε, nonrel	7.83	6.28	5.97
Δε, pseudoatom	-	-	4.78

Figure Legend

Figure 1: Potential curves for the 0_g^+, 0_u^-, and 1_u states of $T\ell_2$ with ${}^3\Sigma_g^-$, ${}^3\Pi_u$, and ${}^1\Sigma_g^+$ curves (computed without spin-orbit coupling) for comparison.

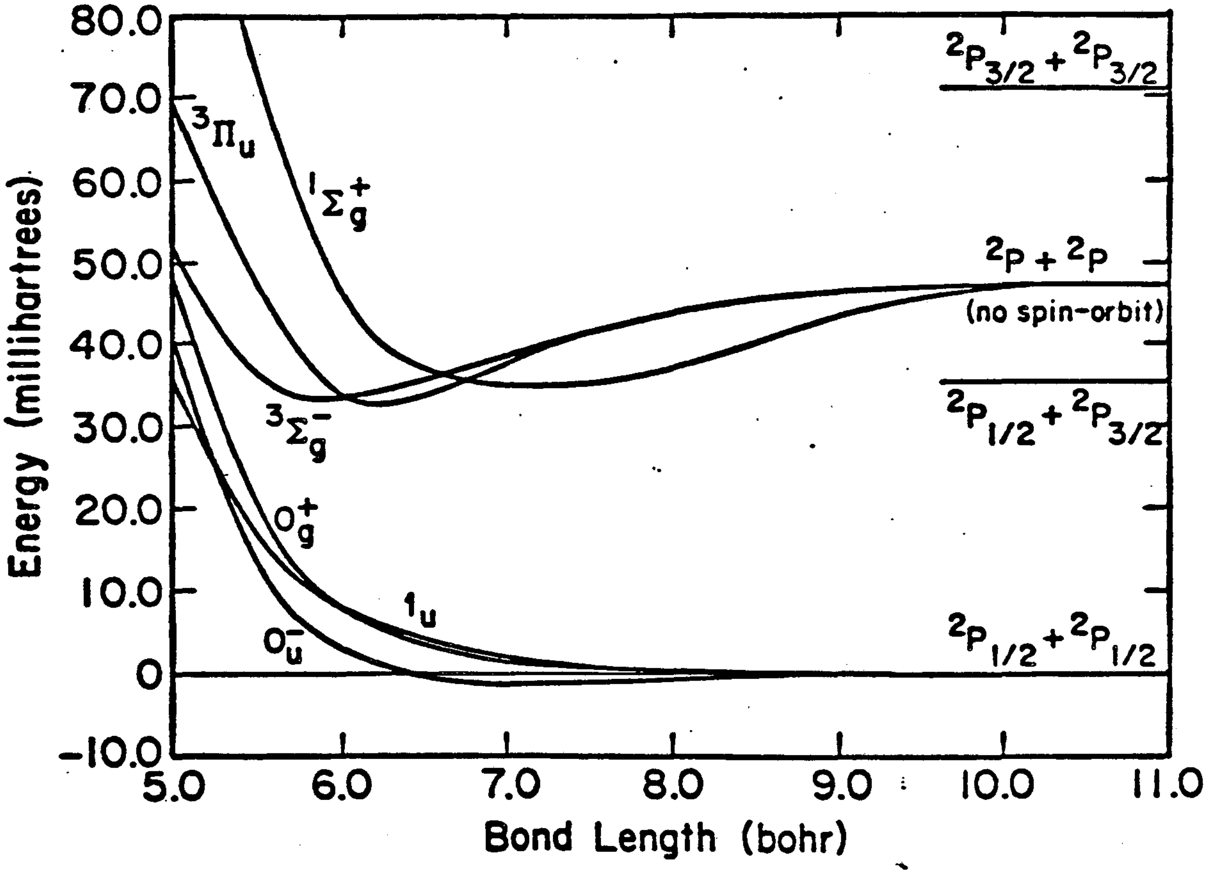

Figure 1. Potential curves for the 0_g^+, 0_u^-, and 1_u states of $T\ell_2$ with $^3\Sigma_g^-$, $^3\Pi_u$, and $^1\Sigma_g^+$ curves (computed without spin-orbit coupling) for comparison.

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