Chem. Rev. **1988**, *88*, 563–594

Relativistic Effects in Structural Chemistry

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Received March 17, 1987 (Revised Manuscript Received July 7, 1987)

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I. Introduction

The two basic theories of modern physics are the theory of relativity and quantum mechanics. While the importance of the latter in chemistry was instantly recognized, it was not until the 1970s that the full relevance of relativistic effects in heavy-element chemistry was discovered.

For very precise calculations, relativistic energy contributions are already needed for H_2^+ or H_2. They increase, for valence shells, roughly like Z^2. Depending on the accuracy achieved in the calculation, they become relevant again around Cu, or perhaps Ag. For the sixth row (around W to Bi), relativistic effects are comparable to the usual shell-structure effects and provide an explanation for much of the basic freshman chemistry of these elements. For the existing actinoids relativistic effects are essential.

The relativistic effects can be defined as anything arising from the finite speed of light, $c = 137.035\,989\,5\ (61)$ au[415], as compared to $c = \infty$. The basic theory is discussed in section II.

Pekka Pyykkö was born in 1941 in Hinnerjoki, Finland, and received his Fil.Kand., Fil.Lic., and Fil.dr from the University of Turku. After working at the Universities of Aarhus, Göteborg, Helsinki, Jyväskylä, Paris XI, and Oulu (1968–1974), he became Associate Professor of Quantum Chemistry at Åbo Akademi in Turku in 1974. Since 1984 he has been Professor of Chemistry at the University of Helsinki, Finland, where he holds the "Swedish Chair of Chemistry", founded in 1908 as a parallel one to Johan Gadolin's former chair, established in 1761. His main interests have been NMR theory and relativistic quantum chemistry.

It has become a tradition to introduce the reader to the qualitative effects of relativity as follows: Due to the relativistic mass increase

$$m = m_0/(1 - (v/c))^{1/2} \tag{1a}$$

m_0 being the rest mass and v the speed of the electron, the effective Bohr radius,

$$a_0 = (4\pi\epsilon_0)(\hbar^2/me^2) \tag{1b}$$

will decrease for inner electrons with large average speeds. For a 1s shell at the nonrelativistic limit, this average speed is Z au. Thus the 1s electron of Hg has a v/c of $80/137 = 0.58$, implying a radial shrinkage by 23%. Because the higher s shells have to be orthogonal against the lower ones, they will suffer a similar contraction. Due to interacting relativistic and shell-structure effects, their contraction can in fact be even larger; for gold, the 6s shell has larger (percental) relativistic effects than the 1s shell.

For readers not convinced by a qualitative argument, we can consider an exactly solvable problem: the hydrogen-like atom with $Z = 80$ in Figure 1. As seen, the contractions are comparable for the three first s shells.

Alternatively, to understand the valence electron effects in a many-electron atom, one can compare (see ref 35) the relativistic (Dirac) and nonrelativistic (Schrödinger) dynamics for the valence electron in a given atomic potential, to study the importance of the direct relativistic effect. The (originally surprising) result[35] was that this is the main effect for the 6s of Au or the 6p* (=$6p_{1/2}$) of Tl. The relativistic change of the atomic potential mattered less than the direct, dy-

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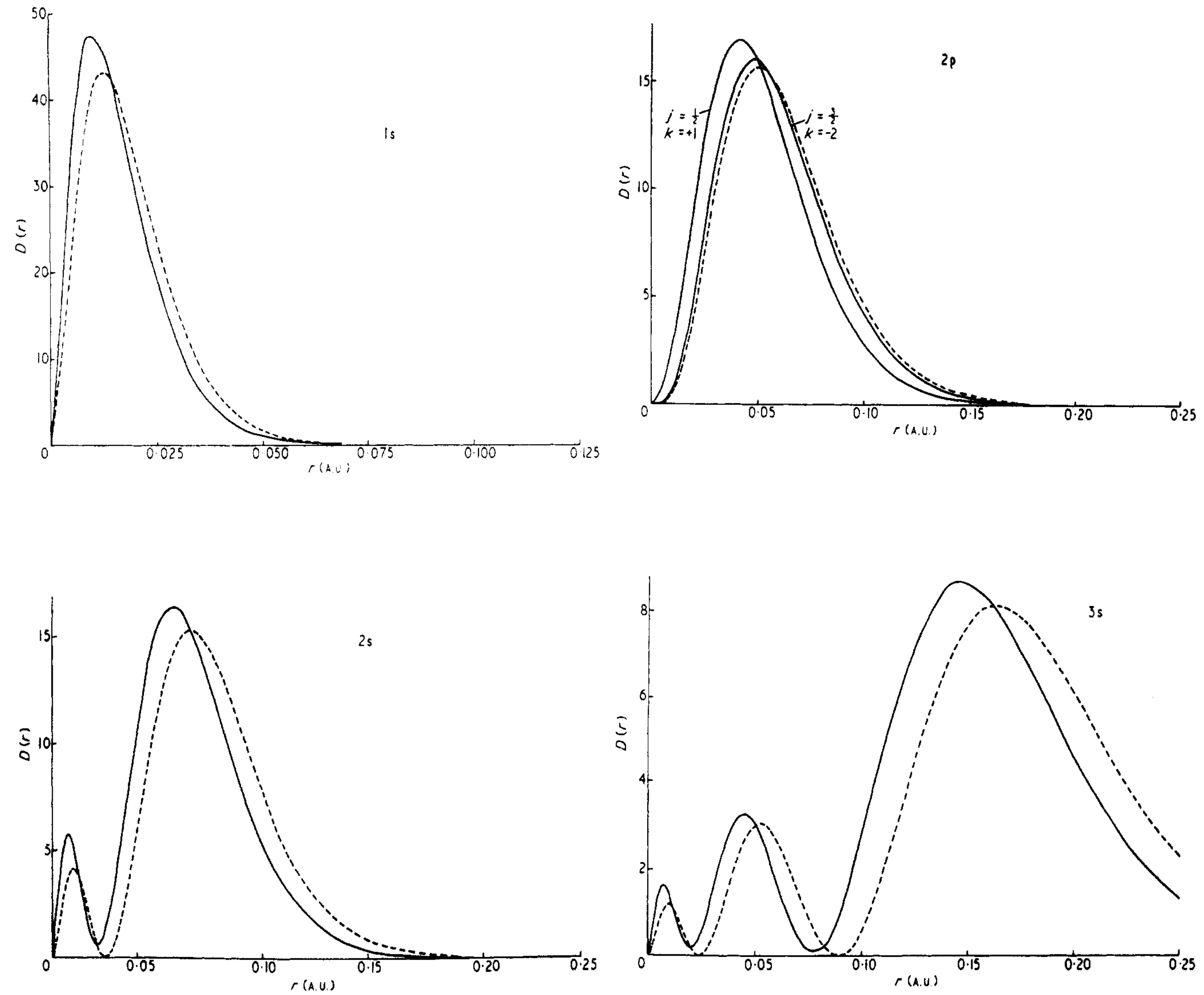


Figure 1. Radial densities for the 1s, 2s, 3s, and 2p states of a hydrogen-like atom with $Z = 80$. The dashed curves are nonrelativistic (NR) and the full curves relativistic. The contractions for 1s, 2s, $2p_{1/2}$, and 3s are of the same order of magnitude while that for $2p_{3/2}$ is much smaller. Reproduced with permission from Burke and Grant.[23b]

namical effect on the valence electron itself.

Second, the $l > 0$ (p, d, f, ...) electrons will suffer the well-known spin–orbit splitting into

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \tag{1c}$$

$$j = l \pm \tfrac{1}{2} \tag{1d}$$

Third, the effective potential for the d and f electrons, which never come close to the nucleus (due to the centrifugal potential $l(l+1)/r^2$), will be more efficiently screened due to the relativistic contraction of the s and p shells. Therefore they will go up in energy and outward radially.[40, 41]

Thus the main effects on atomic orbitals are (1) the relativistic radial contraction and energetic stabilization of the s and p shells, (2) the well-known spin–orbit splitting, and (3) the relativistic radial expansion and energetic destabilization of the (outer) d and all f shells. All three effects are of the same order of magnitude and grow roughly like Z^2.

A recent bibliography[2] on the relativistic theory of atoms and molecules, covering the years 1916–1985, lists 3119 references. Even the reviews are numerous: for the basic theory and atomic calculations one can quote, e.g., Grant,[3] Lindgren and Rosén,[4] or Grant and Quiney[5] and the articles notably by Desclaux or Grant in the conference proceedings.[6–9] The extensive literature on atoms in Russian, including several books, is also covered by ref 2. The reviews on molecular calculations, besides those in ref 6, 7, and 9, include the ones by Pyykkö,[10] Pitzer,[11] Pyykkö and Desclaux,[12] and Christiansen et al.[13]

The attempts to comprehensively review "relativity and the periodic table" from a chemical point of view include Chapter XI of ref 10 and many others,[11–22] including articles in Chinese,[15] French,[16,22] Russian,[17–19] and Swedish[20,21] or material for undergraduate teaching.[21–25]

Presently the elements 1–109 are experimentally known. If any superheavy ones beyond these will be produced, they will be even more strongly relativistic.[26]

The main purpose of the present review is to provide a comprehensive review on the existing data (as of June 1987) on relativistic effects on molecular structures (section III). Other properties are also briefly summarized in section IV. Finally, we mention in section V several cases where relativistic effects *may* be relevant. The relativistic aspects on chemistry are sum-

TABLE I. Calculated 2^3S–2^3P_2 Transition Energies (cm^{-1}) for Helium-like Atoms according to Hata and Grant[30]

Z	NR	Δ_{rel}	total theor[a]	exptl
2	9 230.975 6	2.1603	9 230.791 8	9 230.792 00 (50)
17	135 256.11	28 647.11	162 921.07	162 923 (6)

[a] Including QED.

marized in section VI, especially in Figure 17.

Readers interested in the chemical results but uninterested in the theoretical machinery are urged to jump via section II.B directly to section III.

II. Theory and Methods

A. Fundamental Questions

The most fundamental theoretical level at which heavy multielectrôn atoms can currently be treated is that of numerical, multiconfiguration Dirac–Fock (MCDF) calculations based on the Dirac–Breit Hamiltonian[3–9,28,29]

$$H = \sum_i h_i + \sum_{i>j} (r_{ij}^{-1} + B_{ij}) \tag{2a}$$

$$h_i = c\alpha_i \cdot \mathbf{p}_i + (\beta_i - 1)c^2 - Zr_i^{-1} \tag{2b}$$

$$B_{ij} = -\alpha_i \cdot \alpha_j (\cos \omega r_{ij}) r_{ij}^{-1} + (\alpha_i \cdot \nabla_i)(\alpha_j \cdot \nabla_j)(\cos \omega r_{ij} - 1)/\omega^2 r_{ij} \tag{3}$$

$$\omega = \epsilon_i - \epsilon_j$$

Various quantum electrodynamical corrections, such as vacuum polarization and vacuum fluctuation, can then be added (see ref 6–9). For calculating inner-shell energies they can be substantial; for valence-shell properties the dominant relativistic correction is the one-electron Dirac relativity in eq 2b; both eq 3 and the QED are less important.

Two objections have been raised against this procedure: Sucher[27a] has suggested that projection operators to the electron-like subspace (as opposed to the positron-like one) should be included to prevent a "continuum dissolution" or "Brown–Ravenhall[28] disease". Briefly, this means that electron–electron interaction may mix positive- and negative-energy states, leading to a degeneracy between the bound state and continuum states. It appears, however, that no further projection operators are needed because the electron-like boundary conditions used in the existing numerical programs already accomplish this.[5,29a,b] (See also ref 27b for criticism of the proposed projection operators.)[398]

A second, fundamental reservation could be that eq 2a is not fully Lorentz invariant.[29c] However, the numerical agreement between theory and experiment for atomic energy levels is so good, without exception, that the eventual remaining terms must be small. As an example we quote in Table I results for helium-like atoms by Hata and Grant.[30] These calculations combine the accurate Hylleraas-type nonrelativistic calculations with relativistic effects from a multiconfiguration Dirac–Fock–extended average level (MCDF–EAL) approach, adding the calculated mass-polarization and quantum electrodynamic effects at the end. Note especially that the $Z = 17$ relativistic contribution, Δ_{rel}, must then be correct to at least four figures.

The agreement between theory and experiment remains good for the heaviest elements although the relative size of the terms varies. Thus, the "magnetic" correlation energy involving the magnetic term B_{ij}, (3), exceeds the usual Coulomb correlation (of about −1.21 eV), involving r_{ij}^{-1}, around $Z = 50$ for the 1s2p helium-like atoms.[31] For helium-like uranium the magnetic interaction is large enough to shift[32] the $^3P_0$ state above $^3P_1$.

In a recent paper,[29a] Grant actually questions the need for "ritual obeisance", using words like "a rigorous theory of relativistic atomic structure is not yet available". He also maintains that there are no grounds for not using the Breit operator (3) self-consistently, in contrast to Bethe and Salpeter,[29d] who state that it only should be used as a first-order perturbation. We conclude that the Dirac–Breit Hamiltonian is alive and well.

For chemical purposes, the effects of B_{ij} are only about 3% of those of Dirac relativity for the bond length, R_e, or the force constant k_2 of PbH_4.[33] Thus the central problem for chemists is how to treat the Dirac equation for electrons in molecules.

It is an irony of history that in 1929 Dirac himself,[34a] one year after publishing the Dirac equation[34b,c] and just before stating "Dirac's dictum", thought that relativistic effects would be "of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions" because the average valence-electron speeds are small. The reason he was wrong is twofold: (i) the valence s and p electrons have high speeds in the inner parts (in other words, orthogonality constraints against core states) and (ii) there are indirect relativistic effects, the former being important for the s and p shells and the latter being important for the d and f shells.[35] For the early history of relativistic atomic calculations, see, e.g., ref 2 and 36a.[405]

B. Properties of Individual Atoms

The available literature on atomic calculations up to 1985 is summarized in ref 2. The methods currently available range from single- or multiconfiguration Dirac–Fock (DF) (=relativistic Hartree–Fock (HF); "Dirac" standing for four-component spinors) and the analogous local-density models, such as the Dirac–Slater (DS) one, to various one-component or "quasi-relativistic" approximations (see section II.C). Pseudopotential LCAO approximations to these mostly numerical methods are often used[13] in chemical applications. For atoms, there also exist various $1/Z$ expansion, parametrized model potential, or Thomas–Fermi approaches. The newest development is the use of spline functions to generate a basis of Dirac spinors for many-body theory.[36b,399]

If one reference should be singled out, it would be Desclaux's 1973 compilation[37] of atomic ground-state data (DF data for $Z = 1$–120, HF for $Z = 1$–100). The following trends of chemical interest can be seen already at the atomic level:

Ionization Potentials. The relativistic stabilization and splitting of hydrogen-like systems were found by Sommerfeld[38] using the old quantum theory. The result, incidentally, fully agrees with that for the Dirac equation.[39] The indirect destabilization of Hg 5d

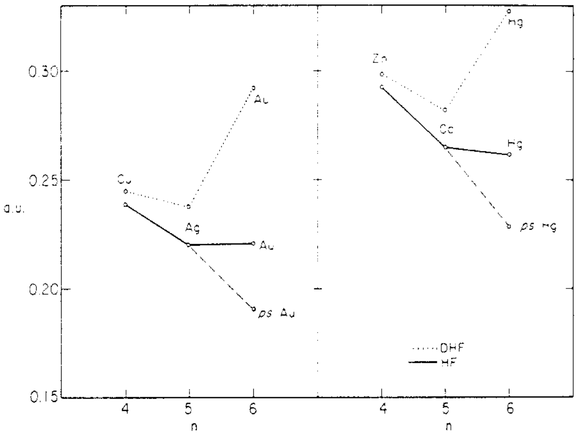


Figure 2. Valence s-orbital energies for the group 11 metals Cu, Ag, and Au and for the group 12 metals Zn, Cd, and Hg. The uppermost dotted curves are the relativistic curves, and the full curves in the middle are the nonrelativistic Hartree–Fock results of Desclaux.[37] The lowest, dashed curves are for the nonrelativistic "pseudoatoms" without 4f electrons.[54] The difference between "real" and "pseudo" is a measure of the "lanthanoid contraction". As seen, it is comparable with the relativistic effects. (Reproduced with permission from ref 54). The experimental IP_1 (7.726, 7.576, and 9.225 eV for Cu, Ag, and Au or 9.394, 8.993, and 10.437 eV for Zn, Cd, and Hg, respectively) parallel the highest dotted curve.

electrons was found by Mayers[40] and that of U 5f electrons by Boyd et al.[41]

The $6s^2$ "inert-pair" effect[42] was quoted as "usually considered" due to relativistic effects in a 1970 review.[43] We have not been able to find earlier references to this proposal. (See section III.E.)

Fricke et al.[14,44,45] and Smith[46] called attention to the local maxima of the IP_1 when a relativistic subshell is filled at $(p_{1/2})^2$ or $(d_{3/2})^4$ (Pb or W). Evidently, both the initial and the final states count. A direct chemical application[46,47] is the interpretation of the chemical stability of the commonly occurring[47] Bi^+ ion.

Another chemical anomaly is the increase of IP_1 of Au or IP_1 and IP_2 of Hg from those of Ag or Cd, respectively. Using Desclaux's tables[37] and Koopmans' theorem, one can directly relate[54] the increase to the relativistic stabilization of the 6s shell, which thus explains the nobility of Au or Hg.[10] It is also striking that the valence-shell relativistic stabilization and contraction show a pronounced local maximum at the coinage metals Cu, Ag, and Au.[48] (see Figure 3). The nature of this interplay between relativity and shell structure for s electrons outside completed d^{10} (and f^{14}) shells has still not been analyzed in detail.

When d electrons are being ionized, relativistic effects *diminish* the IP through the relativistic destabilization of d shells. This was proposed (ref 10, Chapter XI.A.12) as an explanation for the higher maximum valency of 5d elements, compared to their 4d counterparts. The same effect is even stronger between the 5f and 4f elements.

A further question is that of the relative importance of relativity and core polarization. Migdalek and Baylis[49a] find them to be comparable for IP_1 of Au. For Cs, the latter is larger.[49b]

"Secondary Periodicity". Biron[50] noted in 1915 that many physical and chemical properties down a column exhibit a saw-tooth behavior,[51] superimposed on the regular trend down a column. As examples one can quote the tendency of N, As, and Bi to be trivalent while P and Sb are pentavalent, or the difficulties in preparing BrO_4^- [50] or $AsCl_5$. It was proposed by several authors[52] that the first anomaly at row 4 (e.g., As) is caused by a "transition-metal contraction (d contraction)"[52a,b] or "d-block contraction",[52c] caused by an increase of the effective nuclear charge[52d] for 4s electrons due to filling the first d-shell $3d^{10}$. This interpretation was verified by the author[53] using HF or DF calculations on "pseudoatoms" without the d^{10} shell and with Z reduced by 10. (The same ideas had been used by Bagus et al.[54] to study the effect of filling the 4f shell, i.e., the "lanthanoid contraction".) For the second minimum in Figure 4 (e.g., at Bi), relativistic effects and the lanthanoid contraction were actually found to be equally important[53,54] (see Figure 5.)

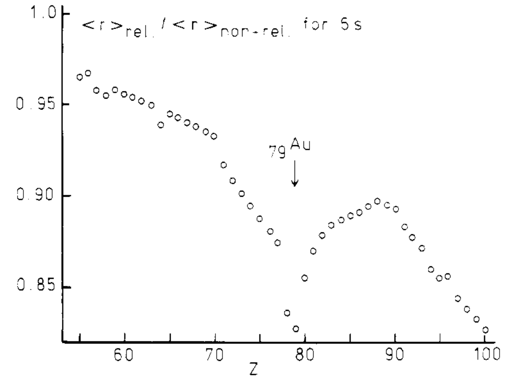


Figure 3. The relativistic contraction of the 6s shell in the elements Cs (Z = 55) to Fm (Z = 100). The numbers are taken from the Dirac–Fock and Hartree–Fock calculations of Desclaux.[37] The contraction increases considerably while the 4f shell is being filled and strikingly when the 5d shell is filled. The pronounced local maximum of the contraction at gold, $(5d)^{10}(6s)^1$, makes Au a unique element, even from this point of view. As discussed in the text, the redox nobility of gold is related to this contraction. An equally strong relativistic contraction is not found until reaching fermium, Z = 100. (Reproduced from ref 12.)

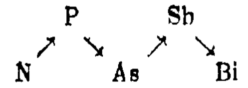


Figure 4. Example of the "secondary periodicity" of Biron. (Reproduced from ref 50.)

Electron Affinities. The very existence of the ionic auride compounds Rb^+Au^- and Cs^+Au^- was related[10,14] to the relativistic stabilization of the Au 6s shell, making gold, in this case, a halogen. Cole and Perdew[55] calculate this increase of the EA to be from 1.5 to 2.5 eV. (See also section III.D.)

Chamizo[56] continues the argument of Smith[46] to explain the small EA of Pb (0.3, 0.37, and 0.95 eV for Tl, Pb, and Bi, respectively) by an existing spin–orbit stabilization of the upper state, $^3P_0$, for Pb while the lower Pb^- ^4S state has none. Nowak et al.[57] considered the relativistic contributions to the EA of groups 1 and 17.

For Hg, one would expect the relativistic stabilization of the $6p_{1/2}$ LUMO to increase EA.[12] Nevertheless, the $6s^26p_{1/2}{}^1$ state of Hg^- only occurs as a resonance, 0.45 eV above the ground state.[58] Mercury anions have been mentioned in discussions of metallic alloys.[59]

Electron Configurations. A further interesting fact is that the relativistic stabilization of s shells and destabilization of d shells lead in many cases to a change of the ground-state electron configuration from $5s^14d^n$ to $6s^25d^{n-1}$, when going from row 5 to row 6 (see Table

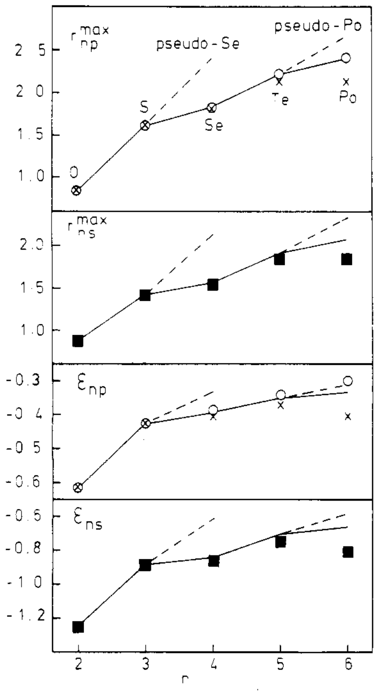


Figure 5. Calculated atomic radii r_{np}^{max} and r_{ns}^{max}, defined as the radius of maximum $(rR)^2$, and the orbital energies ϵ_{np} and ϵ_{ns} for the ground states of group 16 atoms (in atomic units). The curves refer to nonrelativistic results and the points to relativistic results ((■) s; (×) $p_{1/2}$; (○) $p_{3/2}$). "Pseudo-Se" has a nuclear charge of 24 and an empty 3d shell. "Pseudo-Po" has a nuclear charge of 70 and an empty 4f shell. Apart from these two cases, the numbers are taken from ref 37.

TABLE II. Ground-State Electron Configurations of the 4d and 5d Elements in Groups 5–10[a]

	group					
	5	6	7	8	9	10
row 5	Nb	Mo	Tc	Ru	Rh	Pd
	d^4s^1	d^5s^1	d^5s^2	d^7s^1	d^8s^1	d^{10}
row 6	Ta	W	Re	Os	Ir	Pt
	d^3s^2	d^4s^2	d^5s^2	d^6s^2	d^7s^2	d^9s^1

[a] Note that d^5 at Tc is a half-closed shell.

II). (The distance between the d^4s^2 and d^5s^1 configurations is actually smaller for W than for Mo (ref 19, p 148). The point is that their order has been inversed.) This was apparently first noticed by Fricke et al.[14,44,45] and later rediscovered in ref 60. The applications to discuss the chemical difference between Pd and Pt[61,62] are most interesting. Analogous changes occur for the ions ($4d^5$ for Mo^+ but $5d^46s$ for W^+).

A careful MCDF study[63] of $_{103}$Lr shows its ground state to be $7s^27p_{1/2}{}^1$ and not $7s^26d^1$, as suspected earlier.[64]

For discussing quantitatively the question of where between the *LS*- and *jj*-coupled limits a given atomic state is, one will carry out MCDF calculations[65] using *jj*-coupled determinants. Suitable programs are available.[66] For example, for the Pb $6p^2$ configuration a mixture of $(6p^*)^2$, $(6p^*)(6p)$, and $(6p)^2$ ($p^* = p_{1/2}$, $p = p_{3/2}$) may occur. The answer[65] for the $^3P_0$ ground state of Pb is 92.5% $(p^*)^2$ and 7.5% $(p)^2$, closer to the *jj* limit.

When several configurations lie very close, as may happen for an f element, it is of limited chemical interest which one is actually the lowest. It also is good to point out for the more chemical readership that only the total *J*, M_J, and the parity are exact quantum numbers for an atom. Thus MCDF calculations show the $^1S_0$ ground state of Ba, for instance, to consist of 90.6%, 8.3%, and 1.0% of $6s^2$, $6p^2$, and $5d^2$ configurations, respectively.[67] For a summary of the role of d orbitals in the structural chemistry of the "s elements" Ca, Sr, Ba, and Cs, see ref 68 and 69.

Relativistic effects also influence the *Z* value for which d or f orbitals "collapse" from diffuse, outer orbitals to concentrated, transition-metal-like inner ones. For the 5f shell of the neutral atom, this would occur at $Z = 89$ (Ac) and $Z = 90$ (Th) in the HF and DF models, respectively.[70] See also ref 71. The existence of this double-well radial potential was pointed out by Goeppert Mayer.[72]

Atomic Radii. The radius ($\langle r \rangle$, r_{max}, ...) of an atomic valence shell is not an observable nor does it exactly determine the bond lengths of the element (see section II.D). (The relation between the radii of the outermost core shell and the observed ionic radii may be more physically significant.)

Nevertheless it is interesting to note[73] that Cs and Ba are the largest alkali-metal and alkaline-earth atoms, respectively. The relativistic contraction makes the valence shell of Fr and Ra below them smaller than those of Cs and Ba, respectively. It is good to point out that the calculated relativistic molecular bond lengths[68] of the hydrides MH^+ or MH_2 are still some 10–12 pm (10^{-12} m = 0.01 Å) larger for Ra than for Ba. Similarly, the empirical ionic radii[74] for solids are still 6 and 9 pm larger for coordination numbers (CN) 8 and 12, respectively.

Estimates of the lanthanoid contraction for the Ln^{3+} ions will be discussed below.

The various $\langle r^n \rangle$ ($n = -3, -1, 1, 2, 4$, and 6) of all atomic shells are given by Desclaux[37] (DF, $Z = 1$–120; HF, $Z = 1$–100).

The "d-block contraction" and "lanthanoid contraction" are also seen in the atomic radii. A further, obvious trend is the anomalously small size of the first, nodeless shell with each *l* (2p, 3d, 4f). These shells have no inner ones against which they would have to be orthogonal. (In other words, they experience no "primogenic repulsion"[114]). This circumstance keeps the 2p shell as small as the 2s one and thus explains the facile multiple bonding on row 2 (C–O). On row 3, the 3p shell is clearly larger than the 3s one.

C. Available Quantum Chemical Methods for Molecules

1. Fully Numerical Solutions of the Dirac Equation

The most satisfying way to carry out relativistic molecular calculations is to solve the full, four-component Dirac equation numerically, without approximations, for the particular molecular model chosen. For linear molecules, the ϕ variable still separates; for a diatomic, elliptical coordinates may be used for the two other variables in two dimensions ("2D"). Our nonrelativistic, finite-difference programs[75] can then easily be adapted to solve, instead of the usual Dirac equation

$$(h_D - E)\Psi = 0 \tag{4}$$

$$h_D = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta - 1)c^2 + V \tag{5}$$

the second-order Dirac equation

$$[-c^2B^{-1}\nabla^2 - c^2\nabla(B^{-1})\cdot\nabla - ic^2\sigma\cdot(\nabla(B^{-1}) \times \nabla) + V - E]\Psi^{\mathrm{L}} = 0 \quad (6)$$

$$B = E - V + 2c^2 \quad (7)$$

for the "large" two-spinor Ψ^{L} of the four spinor

$$\Psi = \begin{pmatrix} \Psi^{\mathrm{L}} \\ \Psi^{\mathrm{S}} \end{pmatrix} \quad (8)$$

The small component is obtained, if needed, from

$$\Psi^{\mathrm{S}} = cB^{-1}\sigma\cdot\mathbf{p}\Psi^{\mathrm{L}} \quad (9)$$

the electron density

$$\rho(\mathbf{r}) = (\Psi^{\mathrm{L}})^{+}(\Psi^{\mathrm{L}}) + (\Psi^{\mathrm{S}})^{+}(\Psi^{\mathrm{S}}) \quad (10)$$

The second-order equation (6) occurs (for spherical systems) in Dirac's original article.[34b] It was used for H_2^+ and HeH^{2+} [76] or DF calculations on H_2 and HeH^+ [77] by Laaksonen and Grant. Improved results for H_2^+ are reported by Sundholm et al.[78] and "DS" (Dirac–Slater = four-component Hartree–Fock–Slater) ones for the light molecules (LiH, Li_2, BH, ...) by Sundholm.[79]

In these DS calculations, the equation (6) is solved for

$$V = V_{\mathrm{n}} + V_{\mathrm{c}} + V_{\mathrm{x}} \quad (11)$$

where V_{n} and V_{c} are the nuclear potential and electronic Coulomb potential, respectively, and V_{x} is the Slater exchange

$$V_{\mathrm{x}} = -3\alpha(3\rho/8\pi)^{1/3} \quad (12)$$

with α put equal to 0.70, as usual for molecules, and ρ given by eq 10. For a discussion on the relativistic counterparts of eq 12 itself, see reviews 80a and 80b.

In a recent, thoughtful analysis, Cook and Karplus[80c] conclude that for atoms, this model contains no correlation while for molecules, it does, even with the simplest Ansatz (12), because it dissociates to the correct limit, unlike the Hartree–Fock one.

These calculations were already instrumental for pinning down the correct relativistic energy correction of H_2^+ (see Table III). The earlier perturbation theory (PT) calculations used a Hamiltonian whose first, c^2, term is correct but the next, c^4, term is about -10^2 times too large. On the other hand, extensions to many-electron molecules ($N > 10$) will require further technical development.

2. LCAO Four-Component Calculations

For the average chemist, the natural way to approach the Dirac equation (4) would be to use an LCAO approximation for the four--component spinor (8). Some early attempts were less than successful. Then it was realized[5,29,87-93] that the kinetic energy is inaccurate unless the basis functions for the small and large components satisfy eq 9. (The first three papers to do this seem to be ref 88a, 89, and 87b.) Other solutions to this problem have also been considered.[84,88]

DF-LCAO calculations on atoms were pioneered by Kim[94] and Kagawa.[95] Their noninteger STO basis sets did simulate the weak singularity, eq 33, but did not satisfy the "kinetic energy balance" condition, eq 9. For later DF-LCAO calculations on atoms, see ref 96–104, 400 or Table 4.4 of ref 2.

TABLE III. Relativistic Energy Correction E_{R} at the Dirac Level (without QED) for H_2^+ (R = 2 au)

$E_{\mathrm{R}}/10^{-6}$ au	method	ref
−7.38	PT[a]	81
−7.383	PT[a]	82
−7.366	PT[b]	82, 83
−7.36	LCAO	84
−7.3564	2D[c]	76
−7.36	PT	85
−7.366	LCAO	86
−7.3655	2D	78

[a] Using a Darwin Hamiltonian $h_{\mathrm{d}} = B^{-1}\nabla V\cdot\nabla$ (cf. eq 18). [b] Using a correct, purely c^{-2} one, $h_{\mathrm{d}} = c^{-2}\ \nabla V\cdot\nabla = c^{-2}(\pi/2)\sum_i Z_i\delta(\mathbf{r}_i)$. [c] Preliminary.

For doing atoms, the LCAO methods have no obvious merits over numerical ones: the latter are both faster and more accurate.

At this point we also would like to quote the solutions of the "H_2^+-like", one-electron problem using elliptical[105-109] or cylindrical[110] basis functions.

At the time of writing it still seems fair to say that the only DF-LCAO calculations giving some chemical insight were those of Lee and McLean[87,401] on AgH and AuH and perhaps the ones on LiH,[88c] F_2,[90] HCl,[99e] and GeH_4.[93a]

3. Dirac–Fock One-Center Expansions

This "DF–OCE" method can be regarded as a slight extension of the numerical, atomic DF codes to hydride molecules, MH_n, by expanding the potential of the protons in spherical harmonics and solving the radial functions of the various symmetry functions by numerical methods. The method is fully relativistic, is fully self-consistent (not freezing any core orbitals), and uses the full (nonlocal) exchange. First proposed by Mackrodt,[111] it was used by Desclaux and Pyykkö to obtain much of the early insight on relativistic effects on bonding (ref 112a,b, 113a–d, 68, and 114 formed parts 1–8 of the series). Some further calculations were reported in ref 69 and 115. The method was reviewed by Desclaux.[116] For an application on electric polarizabilities of ns^1 and ns^2 atoms, see ref 117a. One quasi-relativistic HFS–OCE calculation has also been reported.[117b] For further production work, this method has now been superseded by others.

From nonrelativistic work,[118a,b] the OCE model is known to give reasonable bond lengths and force constants. The calculated bond lengths furthermore converge smoothly to the Hartree–Fock limit as a function of l_{max}, the highest spherical harmonic included.[118c] Thus the obtained relativistic corrections can also be assessed to be semiquantitatively correct.

(While the radial basis used is "infinite", the angular basis is very limited. The resulting bad angular cusp on the off-center nuclei may cause the molecular total energy near R_{e} to be quite high, in fact often above that of the component atoms,[118d] a circumstance repeatedly mentioned by Malli.[119])

4. The Dirac–Slater Discrete Variational Method

The DS–DV method was developed by Rosên and Ellis.[120] For reviews, see ref 121a–d. The four-component basis functions, ϕ;, used in this method are numerical DS ones for the atoms, in some chosen state, or their combinations for a given molecular symmetry.[121a] The molecular integrals between them are calculated in a numerical, 3D grid

$$h_{ij} = \sum_k w_k \phi_i^{+}(\mathbf{r}_k) h_{\mathrm{D}} \phi_j(\mathbf{r}_k) \tag{13}$$

w_k being the weight factor for grid point $\mathbf{r}_k$ and h_{D} the Dirac Hamiltonian (5) for the potential (11). More sophisticated exchange-plus-correlation potentials can also be used and improved the calculated IP for the halides LnX_3.[121a].

The diagonalization

$$(\mathbf{h} - E_i S)\mathbf{c}_i = 0 \tag{14}$$

yields the MOs

$$\psi_i = \sum_j c_j \phi_j \tag{15}$$

The obtained one-electron or total energies have a numerical accuracy of a fraction of an electronvolt. Adequate for fertile studies of photoelectron or optical spectra and bonding,[120,121] this precludes calculations of potential energy curves, apart from a recent application on N_2.[122] Several superheavy collision systems have also been studied.[121b,122b]

5. Dirac–Slater Multiple-Scattering Method

As in the usual multiple-scattering (MS) method, one divides the space into (eventually overlapping) spheres, one around each atom and one around the molecule. The (1D) radial functions are solved numerically in each sphere. Plane waves are used between spheres. For reviews, see ref 123a–d. The theory was developed in ref 123e–k. Its applications include ref 123l–126.[406]

The method has given insight into photoelectron spectra and bonding in transition-metal compounds,[124] zero-field splittings,[125] or hyperfine tensors and **g** tensors.[126] Potential energy curves have not been reported.

6. Quasi-relativistic Multiple-Scattering Method

This method resembles the previous one, except that the full, four-component Dirac equation is replaced by some approximate one-component equation (see section II.C.13). A program is available from QCPE.[127] The method has been used for interpreting photoelectron spectra and bonding by Hemstreet,[128] Boring and Wood,[129] Rösch,[130] Johnson,[131] Chermette et al.,[132] Bursten,[133] Heera et al.,[134] Topol' et al.,[135] Gagarin et al.,[136] and others.[137] For a summary, see Table 7.6 of ref 2 or ref 132c.

One result directly concerning structural chemistry has been published: Michels et al.[138] reported potential energy curves for Hg_2^{+}.

7. Perturbative Hartree–Fock–Slater Method

This method, developed at the Free University of Amsterdam,[139] is an extension of Ellis' nonrelativistic discrete variational method using the Slater exchange (12). For reviews, see ref 140 and 148h. The results comprise ref 69 and 141–148.

In this method, one calculates the first- and second-order energies, $E^{(1)}$ and $E^{(2)}$, of the relativistic mass-velocity, Darwin, and spin–orbit operators (in au)

$$h_{\mathrm{pert}} = h_{\mathrm{m}} + h_{\mathrm{d}} + h_{\mathrm{so}} \tag{16}$$

$$h_{\mathrm{m}} = -\nabla^4/8c^2 \tag{17}$$

$$h_{\mathrm{d}} = \nabla^2 V/8c^2 \tag{18}$$

$$h_{\mathrm{so}} = s\cdot(\nabla V\cdot\mathbf{p})/2c^2 \tag{19}$$

V being the total one-electron potential (11). The nature of the basis functions (free-atom HFS orbitals) apparently prevents any troubles in using (16) to second order. As alternative forms for a local potential V, one may use

$$h_{\mathrm{m}} = (E - V)^2/2c^2 \tag{17'}$$

while for a nuclear Coulomb potential, $-Z/r$,

$$h_{\mathrm{d}} = \pi Z\delta(\mathbf{r})/2c^2 \tag{18'}$$

A transition-state procedure has been developed for calculating binding energies (potential energy curves) between atoms or other fragments. This method has given plenty of insight into bonding, both for photoelectron spectra and especially concerning the nature of the relativistic bond contraction.[69,148f,g]

Changing the Slater exchange, eq 12, for another density functional provided more modest values for the dissociation energy (D(M–M)) of metal–metal bonds.[148i]

8. Other Density-Functional Approaches

The DF atomic densities can be used in Gordon–Kim-like approaches to interatomic potentials.[149–154] The results are also needed in theories of ionic solids.[154–157]

Density-functional approaches with a quasi-relativistic Hamiltonian have been tested on molecules.[158] (The pseudopotential ones are included in the next section.)

Relativistic Thomas–Fermi atoms have been considered for a long time.[159] The only available result on molecules seems to be a curious one by March[160] that the relativistic bond contraction for XH_4, $Z_X \rightarrow \infty$, would be negligible.

9. Pseudopotential Methods

This method has given more results for molecules than any of the others. For reviews on relativistic pseudopotential work, see ref 13 and 161–170. The central idea of a pseudopotential method is to omit the frozen inner shells, and the corresponding nodes in an atomic valence wave function ψ_{nl}, by considering instead the eigenvalue problem for a nodeless one-component pseudo wave function ϕ_{nl};

$$(F_{\mathrm{nl}} - E_{\mathrm{nl}})\phi_{\mathrm{nl}} = 0 \tag{20}$$

where the Fock operator for atom A is

$$F_{\mathrm{nl}} = -\nabla^2/2 - Z/r + U^{\mathrm{A}} + J_{\mathrm{nl}} - K_{\mathrm{nl}} \tag{21}$$

$$U^{\mathrm{A}} = \sum_l U_l(r)|lm_l\rangle\langle lm_l| \tag{22}$$

Here Z is the (true) nuclear charge and U is the pseudopotential while J_{nl} and K_{nl} are the Coulomb and exchange operators *between the valence electrons*. An essential step was the adoption of the correct valence normalization

$$\phi_{\mathrm{nl}} = \psi_{\mathrm{nl}},\ r > a \tag{23a}$$

$$\phi_{\mathrm{nl}} = \chi_{\mathrm{nl}},\ r < a \tag{23b}$$

χ_{nl} being some polynomial, and a a cut-off radius. This approach is known in chemistry as a "shape-consistent" pseudopotential and in physics as a "norm-conserving" pseudopotential.

In a pseudopotential calculation, both the number of explicitly treated electrons and the number of basis functions needed for one of them are drastically diminished. The starting point thus is an all-electron relativistic atomic calculation, either a DF or DS four-component one, with subsequent averaging

$$U_l = (2l + 1)^{-1}(lU_{l,l-1/2} + (l + 1)U_{l,l+1/2}) \quad (24)$$

or a quasi-relativistic one-component calculation. Empirical pseudopotentials, fit to atomic spectra, can also be used. Core polarization can be described by further terms in the potential. The Fock operators for molecules ABC ... combine a

$$U = U^{\mathrm{A}} + U^{\mathrm{B}} + \ldots \quad (25)$$

The dynamics of eq 20 are nonrelativistic, but the orthogonality against the relativistic core states, due to the U, reproduces the relativistic behavior. If spin–orbit splitting is desired at some stage, the one-component average (24) may be perturbed by

$$U_{\mathrm{so}} = \sum_{l=1} \Delta U_l [l|l, l + \tfrac{1}{2}\rangle\langle l, l + \tfrac{1}{2}| - (l + 1)|l, l - \tfrac{1}{2}\rangle \times \langle l, l - \tfrac{1}{2}|]/(2l + 1) \quad (26)$$

$$\Delta U_l = U_{l,l+1/2} - U_{l,l-1/2} \quad (27)$$

The available pseudopotentials have been summarized.[171,188k,191b,240c,d] The molecular applications comprise ref 61, 62, 172–253, and 406.

10. First-Order Perturbation Theory

The oldest and most straightforward way of estimating relativistic corrections to molecular energies is to calculate the expectation values of the operator (16) using some ab initio wave function, eventually treating the electron–electron terms explicitly and not via V_c and V_x in (18) and (19). This approach can be used for studying molecular fine structure (for reviews, see ref 255–256), potential energy curves,[257-270,402,403] dipole moments (in a finite-field approximation),[263,268,270b] or molecular excitation energies.[271]

QED terms may also be added.[257c,d,260b,262a]

11. Semiempirical Methods

The relativistic effects for row 6 or below are so large that it is fully motivated to include them in the parameters of extended Hückel theory (EHT) or other semiempirical methods. For parameters deduced from experimental atomic spectra, this evidently already is the case; experiments are relativistic. A quasi-relativistic, one-component average of atomic DF data may also be used,[272-275] in particular for the radial parameters. Especially for actinoids the necessity of relativistic radial functions was recognized quite early.[273,404]

Qualitatively new aspects are introduced if the spin–orbit splitting is included in the scheme.[276-289] In particular, the nonrelativistic symmetry orbitals must be replaced by their relativistic counterparts. The effects on photoelectron spectra may be conspicuous.

Charge-iterative schemes employing spin–orbit-split, two-component functions have also been presented.[290,291] The roughly CNDO-level scheme of ref 292 works in jj-coupling but uses nonrelativistic radial functions.

One also can regard the EHT as a scheme for extrapolating atomic results to the molecular domain. By comparing HF versus DF, one then can study relativistic effects for light molecules as well. This was the philosophy behind the relativistc extended Hückel theory ("REX"). References 293a–j form parts 1–10 of the series. Other applications also exist.[144,294,295] The original REX program[296] has been improved twice: Rösch[297,298] speeded it up by using quaternionic algebra. Charge iterations[293i] were added in the latest version.[299]

In the REX method, the energy parameters h_{ii} and the radial parameters are optained for jj-coupled atomic states from ab initio (DF/HF or DS/HFS) calculations for atoms. The off-diagonal ones are obtained from the usual approximation

$$h_{ij} = (K/2)(h_{ii} + h_{jj})S_{ij} \quad (28)$$

or the other usual alternatives and finally the eigenvectors $\mathbf{c}$ and eigenvalues E are obtained from

$$(\mathbf{h} - E\mathbf{S})\mathbf{c} = 0 \quad (29)$$

The ad hoc formula (28) was criticized by Lyudchik et al.[300]

The borderline between "semiempirical" and "pseudopotential" methods is fluid; we quote ref 301 here. Quasi-relativistic CNDO results have been presented by Boča,[302a] and INDO results for lanthanoid complexes have been presented by Culberson et al.[302b] The efforts to construct ZDO-level jj-coupled methods have not yet been brought to fruition. A more detailed review on the relativistic, semiempirical approaches for molecules is scheduled for ref 303.

The EHT band structure programs used by Hoffmann's group[304] are nonrelativistic or, at most, quasi-relativistic. A band-structure REX program has been written by Lohr.[305]

12. Miscellaneous

Relativistic crystal-field theory is discussed in ref 2 (Table 7.12) or ref 10 and will be omitted here.

The "diatomics in molecules" (DIM) method uses as input experimental atomic data and is in this sense "relativistic". Results for coinage-metal trimers are given in ref 306a.

To the extent that Dewar's MNDO parameters for elements like Hg[306b] or Pb[306c] are deduced from experimental molecular data, they also should simulate relativistic effects.

McLean[307] has studied relativistic effects by comparing correlated, large-scale nonrelativistic ab initio calculations on AgH, AuH, and Ag_2 against experiment. To the extent these calculations represent the nonrelativistic limit, whatever differences remain, they must be relativistic.

Malli and Pyper[119b] presented an interesting hybrid, numerical + LCAO method in which the heavy atom is described by numerical DF wave functions orthogonalized against LCAO spinors, used for light ligands. The basis was augmented by additional heavy-atom valence AOs. Both SCF-level and intra-valence-shell correlated versions were constructed. Due to a better "deep core", a lower total energy was then obtained than in earlier LCAO[87a] all-electron work. The valence basis set was still relatively small and only limited CI was included. The SCF-level bond length contraction for AuH (see Table IV) is comparable with the earlier values. The significant 5d–6s hybridization[215d] was also confirmed.

The double-group symmetries of the relativistic molecular orbitals will not be discussed in the present work.

13. *Quasi-relativistic Hamiltonians for ab Initio Calculations*

We have purposely left at the end the question, could usual LCAO ab initio calculations be completed by some quasi-relativistic (QR) Hamiltonian, accounting during the SCF cycles approximately for the direct and indirect relativistic effects.

For atomic calculations such a recipe exists.[308] As shown by Dirac[34b] himself, for spherical potentials V, the radial equation for the large component, $G(r)$, can be transformed to the exact second-order form

$$\left[-\frac{1}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+V+\frac{l(l+1)}{2mr^2}-E-\frac{(V-E)^2}{2mc^2}-\frac{1}{2mB}\left(\frac{\partial}{\partial r}+\frac{\kappa+1}{r}\right)\right]G=0 \qquad (30)$$

with $B = E - V + 2mc^2$. The substitution $G = r^{-1}B^{1/2}P$ transforms it to[34b]

$$\left[h_{\mathrm{nr}}-E-\frac{(V-E)^2}{2mc^2}-\frac{1}{2B}\frac{\kappa}{r}\frac{\partial V}{\partial r}+\frac{1}{4B}\frac{\partial^2 V}{\partial r^2}+\frac{3}{8B^2}\left(\frac{\partial V}{\partial r}\right)^2\right]P=0 \qquad (31)$$

Equation 31 is sometimes referred to as the Mott–Massey equation while (30) is often called the Cowan–Griffin[309] equation. It was shown in ref 309 that one can use (30) as a quasi-relativistic equation in a HF scheme. While the exact Dirac equation has only a part of its norm in the large component $G(r)$, the approximation consists of putting all the norm in $G(r)$, then corresponding to the nonrelativistic radial function, $R(r)$. Cowan and Griffin also averaged the states

$$j = l + \tfrac{1}{2}, \qquad \kappa = -l - 1 \qquad (32a)$$

$$j = l - \tfrac{1}{2}, \qquad \kappa = l \qquad (32b)$$

thus obtaining a one-component, quasi-relativistic equation. The correct boundary condition

$$\lim_{r\to 0} R = r^{\gamma} \qquad (33)$$

$$\gamma = (1 - (\kappa Z/c)^2)^{1/2} \qquad (34)$$

must be used in the numerical integration. The "quasi-relativistic multiple-scattering method" in section II.C.6 is based on the same idea. The exact $G(r)$ are not orthogonal. Instead

$$\int_0^{\infty} (G_iG_j + F_iF_j)r^2\,\mathrm{d}r = \delta_{ij}$$

Putting the R_i orthogonal is therefore another approximation.[311b]

The theoretical justification of this method is not clear but the results, for heavier atoms, must be deemed good. In particular, the second-order, self-consistent relativistic effects are then approximately included. For light atoms the QR Hamiltonian may actually be worse than the simple Pauli theory, eq 16. If the Darwin operator h_{d} (18) is replaced by $c^2B^{-1}h_{\mathrm{d}}$, the c^{-2} correction remains unchanged, but the c^{-4} one is about -1×10^2 times wrong[78] for H and H_2^+. In that case B is a "decoration" that should rather be omitted.

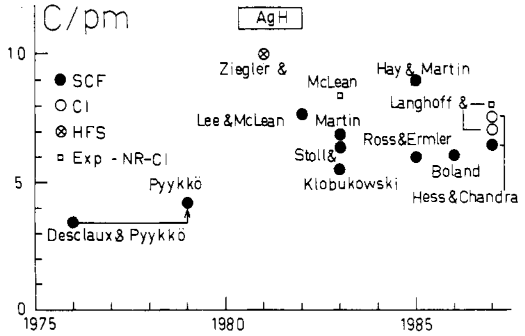


Figure 6. Relativistic contraction of the bond length of diatomic AgH versus the year of publication. The references can be found in Table IV.

Barthelat et al.[310] introduced a slightly different equation and could make it work using at the origin contracted LCAOs, amounting to (33). More approximate equations have been studied by Karwowski et al.[308,311]

After several unsuccessful computations, Hess[312a] has now found a rather complicated "no-pair" Hamiltonian that gives sound results. The derivation is based on the equations of Douglas and Kroll.[312c] The method has been tested on Ag, AgH,[312b] and hydrogen-like systems. See also ref 313. Attempts in the same direction, so far only tested on hydrogen-like systems, are reported by Durand et al.[314]

D. Effects on Bond Lengths

Apart from the work on H_2^+[81], the first paper studying relativistic effects on the bond lengths in heavy-element compounds seems to be that of Desclaux and Pyykkö.[112a] Contractions of about 6% and 7% were found for PbH_4[112a] and AuH,[112b] respectively, using the DF–OCE methods. Other methods (pseudopotentials) subsequently gave slightly larger values of the same order of magnitude. The developments for AgH are shown in Figure 6. The bond length contraction being comparable with the orbital contraction, it was thought, without further proof, to be caused by it.[12]

A "Dutch revolution" occurred in 1980 when Ziegler, Snijders, and Baerends[148f,g] found that they could reproduce the effect by using first-order perturbation theory, just calculating

$$E^{(1)} = \langle i|h_{\mathrm{pert}}|i\rangle \qquad (35)$$

(eq 16), using the nonrelativistic, uncontracted orbitals. The second-order energies, $E^{(2)}$, were not negligible but depended more slowly on the bond length R (see Figures 7 and 8). The conclusion was confirmed by Snijders and Pyykkö[115] using frozen, "pseudorelativistic" orbitals for AuH and TlH in the DF–OCE method (see Figure 9).

Breaking up the $E^{(1)}$ (35) for a valence molecular orbital

$$\psi_i = \phi_{\mathrm{v}} + \phi_{\mathrm{c}} \qquad (36)$$

where ϕ_{v} and ϕ_{c} are valence and core AOs, respectively,

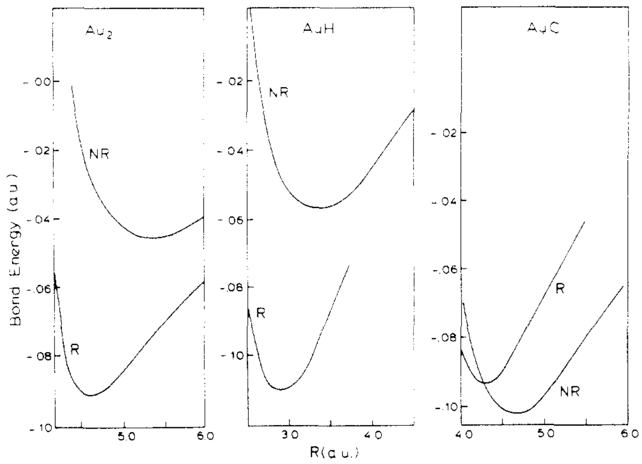


Figure 7. Calculated nonrelativistic (NR) and relativistic (R) potential energy curves for Au_2, AuH, and AuCl. (Reproduced by permission from Ziegler, Snijders, and Baerends.[148f])

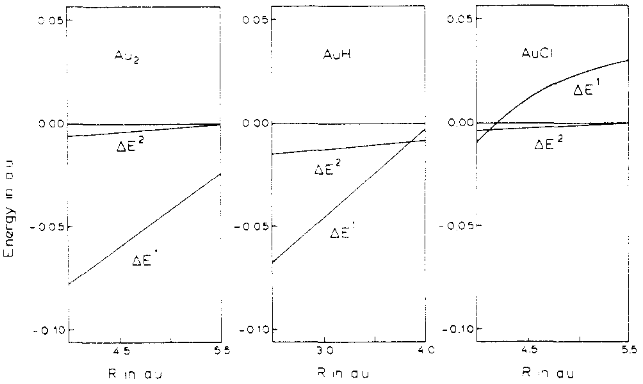


Figure 8. Dependence of the first- and second-order relativistic energies on the bond length.[148f]

into the valence–valence, valence–core, and core–core contributions

$$E^{(1)} = E_{vv}^{(1)} + E_{cv}^{(1)} + E_{cc}^{(1)} \quad (37)$$

it was further found[148g] that the driving force behind the bond contraction was $E_{cc}^{(1)}$, the diagonal core–core contribution in a valence MO.

Consider as an example the CsH molecule[69] with the single valence MO

$$\sigma = c_1\phi_{6s} + c_2\phi_{5d} + c_3\phi_{1s} + c_4\phi_c \quad (38)$$

ϕ_c standing for the Cs subvalence 5s and 5p AOs. If R decreases, the overlap $\langle 1s|5s\rangle$ increases, which increases c_4 and therefore makes the (negative) $E_{cc}^{(1)}$ larger. (The negative $\langle h_m\rangle$ dominates over the positive $\langle h_d\rangle$ in $E_{cc}^{(1)}$.) Therefore the bond contracts.

Alternatively one could say that the kinetic energy increase in the repulsion between the two atoms is diminished by the relativistic terms.

Adding the 5d AOs to the basis makes the contraction smaller. Again, it is *not* related to a cancellation of s + p contractions and d expansions as thought earlier.[113b] Instead, putting $c_2 = 0$ in eq 38 makes c_3, and therefore c_4, larger and increases the contraction. Putting $c_2 \neq 0$ diminishes c_3 and hence c_4 and makes the contraction smaller.[69] Taking stock, the relativistic contraction of orbitals and the relativistic contraction of bond lengths are two parallel but largely independent effects.

Martin[267] and Katriel et al.[265] later arrived at the same conclusion. Several perturbative calculations of bond length contractions have appeared[261,263-270,402,403] (for a summary, see Table IV).

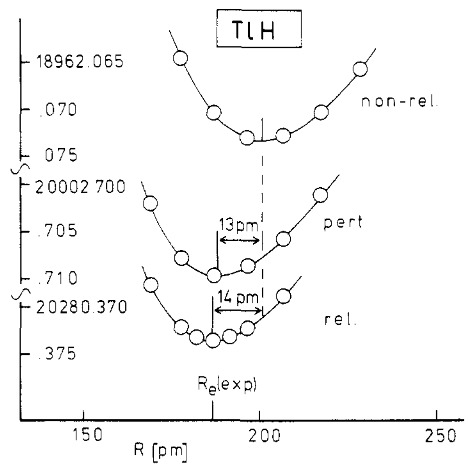


Figure 9. Calculated nonrelativistic and relativistic OCE potential curves for TlH.[113a] The first-order perturbation curve[115] reproduces most of the relativistic contraction. (Reproduced with permission from ref 115.)

Schwarz[315,316] does not disagree with this explanation but argues that an alternative interpretation is possible.

Define the relativistic contraction

$$C = R_{NR} - R_R \quad (39)$$

$$C/\text{percent} = 100 \times ((R_{NR} - R_R)/R_{NR}) \quad (40)$$

Following Schwarz,[316] one can write, to first order in c^2

$$C = k^{-1}(\partial^2 E/\partial R\, \partial(\ln c^2)) \quad (41)$$

where the force constant

$$k = \partial^2 E/\partial R^2 \quad (42)$$

The (by now) accepted "Dutch" interpretation of the contraction then relies on

$$C = k^{-1}\partial\langle\psi|\partial H/\partial(\ln c^2)|\psi\rangle/\partial R \quad (43)$$

while Schwarz' alternative is to look at

$$C = k^{-1}\partial\langle\psi|\partial H/\partial R|\psi\rangle/\partial(\ln c^2) \quad (44)$$

The difference appears clearer in the forms

$$\partial^2 E/\partial(c^2)\,\partial R = \langle\psi|\partial^2 H/\partial R\,\partial(c^2)|\psi\rangle + \langle\psi|\partial H/\partial(c^2)|\partial\psi/\partial R\rangle + cc \quad (45a)$$

$$\partial^2 E/\partial(c^2)\,\partial R = \langle\psi|\partial^2 H/\partial R\,\partial(c^2)|\psi\rangle + \langle\psi|\partial H/\partial R|\partial\psi/\partial(c^2)\rangle + cc \quad (45b)$$

The last terms of the traditional form (45a) involve the change of the wave function with distance and the perturbation (16)

$$\partial H/\partial(c^2) = -c^2 h_{pert} \quad (46)$$

while Schwarz' alternative form (44) involves the relativistic orbital contraction, $\partial\psi/\partial(c^2)$.

The origin of the bond contraction in pseudopotential calculations was considered by Christiansen and Ermler[188d] and further analyzed by Schwarz,[316] who concludes that the *first* term of eq 44, in particular the part arising from the *effective nucleus–electron potential*, V_{ne}^{eff}, would now be the most important one:

$$C \cong k^{-1}\langle\psi|\partial^2(V_{ne}^{eff})/\partial R\,\partial(\ln c^2)|\psi\rangle \quad (47)$$

III. Molecular Geometries

A. Bond Lengths

The available, explicit studies of relativistic effects on bond lengths are collected in Table IV.[402,403,411]

The results from the various methods are of the same order of magnitude but, as seen from Figure 6, few definitive benchmarks exist. The 2D value[79b] for H_2^+ may be one.

To the extent that spin–orbit effects can be neglected and first-order perturbation theory suffices, the calculations[270a,216b] on Cu_2 would seem to have a chance of being near a definitive value. The final deviations from experiment are 1 and 3 pm, and the relativistic contractions are 4 and 3.8 pm for ref 270a and 216b, respectively. The recent P-CPF work[216c] on AgH is of similar quality. The contraction is 7.1 pm, $r_{\text{calcd}} = 162.8$ pm and $r_{\text{exptl}} = 161.8$ pm.

Martin[220b] finds that, for Ag diatomics, f basis functions considerably improve the description of the 4d shell correlation at the fourth-order Møller–Plesset level.

Correlation effects slightly decrease C for Cu_2,[270a] GeH,[270b] and Ag_2[177a] but slightly increase it for AgH[312b] and CsH.[217f] The "P-HFS" C values for heavier elements are at the high end. In addition to CuH and AgH, inclusion of relativistic effects clearly improves agreement with the experimental R_e for CuO, Cu_2, AgCl, Ag_2,[148g] $HfCl_4$, PtH, AuH, Au_2, HgH^+, $HgCl_2$, Hg_2^{2+}, and TlH.

It is interesting to note that the experimental bond lengths are shorter for AuH than for AgH (152.4 and 161.8 pm, respectively) while diatomic Au_2 and Ag_2 are of the same size (247.2 and 248.2 pm, respectively).

The effect almost always seems to be a contraction; the only reasonably certain exceptions for heavy-element compounds are Tl_2^+[241a] and Tl_2.[188g] In both cases relativistic effects largely destroy the bond: for TlH^+ the Tl^+ $6s^2$ dissociation limit is relativistically stabilized by the s AO contraction, and for Tl_2 the atomic $(6p_{1/2})^1$ ground states are spin–orbit stabilized. The effects are very large because k in eq 42–47 is small. In general, a method underestimating k should overestimate C.[269]

The monohydrides around group 3 (like YH[216c]) also seem to show slight expansions (0.8 pm for the ground state of YH).

Z^2 Fits. Relativistic effects roughly scale as Z^2. The contractions for the group 11, 13, and 14 hydrides (plus H_2^+) were therefore fit in 1979 to[68]

$$C/\text{pm} = c_Z Z^2 \tag{48}$$

$$c_Z = 17\ (6) \times 10^{-4}$$

An inspection of Table IV however shows substantial dependence on the group, roughly following Figure 3 (minima at groups 1 and 18, a local, "gold maximum" at the coinage metals, group 11). A dependence on the electronic state is also evident; see the data for AgH[312b] and PtH.[177i] Similarly, for NiH ($X^2\Delta$), the particular CI mixture has a large effect.[263]

To obtain a better rule of thumb we therefore consider in Table V the relativistic contraction of single-bond covalent radii separately for each group. (Some cases are problematic: for Hg, contractions of r_{cov} vary from 13 pm for $Hg(CH_3)_2$ to about 23 pm for Hg_2^{2+} or Hg_2^+). As seen from Table V, the c_Z values decrease from about 0.003 for group 11 to about 0.001 for group 1 on the left and to about 0.0003 for group 17 on the right. In groups 13 and 14, the few data available for rows 2 (C) and 3 (Al, Si) (without filled d shells) are a factor of 2 smaller than those for rows 4 and 5.

Covalent Radii for Electropositive Metals. An attempt was made in ref 113d and 68 to extract for a number of electropositive elements covalent radii that would be appropriate for discrete molecules. The starting point was Pauling's halogen radii, 64, 99, 114, and 133 pm for F, Cl, Br, and I, respectively. These halide radii are consistent with the metal atom radii in Table VI. A corresponding sp^3 carbon radius for M–C bonds is about 97 pm, and the hydrogen radius is 58 pm. The difference $r_C - r_H$ is 39 pm for the present radii and 47 pm for the Pauling ones ($r_H = 30$, $r_C = 77$ pm).

Pauling's[321,322] radii are different for two reasons: First, the coordination numbers are often different (e.g., 4 instead of 2 for group 12). Second, in Pauling's recent work,[323] M–H, M–C, and M–P bonds only were considered, with the traditional H, C, and P radii of 30, 77, and 110 pm, respectively. These smaller ligand radii give larger metal radii than the present ones. Instead of H, C, and P, the present metal radii are consistent with the halogen radii. Then the metals are smaller and the "anionic" r_H and r_C become larger. Table V gives an idea of the relativistic contractions inside these, in themselves purely operational, radii, r_{cov} in Table VI.

Trends for Main Groups. Haaland[324] considered the experimental bond lengths to H, CH_3, and Cl for elements, E, belonging to groups 2 and 12–17. Along a row, the E–C bond length decreased for rows 2 (Li–F) and 3 (Mg–Cl), was stationary for rows 4 and 5, and *increased* for row 6 (Hg to Bi). Haaland suggested that in rows 4 and 5 the gradually decreasing d-block contraction (from Zn to Br, say) would cancel the normally expected decrease of the covalent radius. The E–H decreases from E = Zn to E = Br, while E–C and E–Cl are roughly constant, perhaps due to the absence of a repulsive core in hydrogen. Haaland[324] suggests that the increase of E–C from E = Hg to E = Bi in row 6 could be due to a simultaneously decreasing lanthanoid + d-block contraction and relativistic effects when moving away from the "gold maximum". Further evidence for the decrease of the d-block + lanthanoid contractions from group 13 to group 17 was provided by the straightening out of the "secondary periodicity".[324]

Lanthanoid Contraction. When the lanthanoid series is crossed from $La^{III}(4f^0)$ to $Lu^{III}(4f^{14})$, the ionic radii (ref 74, CN = 8) decrease by 18.3 pm. The analogous decrease of the Ln–Br distances in gaseous $LnBr_3$ molecules is 18 pm.[326] Waber and Cromer[327] calculated a decrease of the DS $r_{\max}(5p)$ of 19 pm from La^0 to Lu^0 (or 18.7 pm from La^{3+} to Lu^{3+}). For the $^1\Sigma$ states of the diatomic hydrides, the jump from LaH[328a] to LuH[328b] similarly is 18.9 pm.

It is interesting to ask how much of this decrease does come from relativistic effects.[11,68,113d,114] The available answers are collected in Table VII. The molecular values suggest that about 2 pm or of the order of 10% of the lanthanoid contraction would come from relativistic effects. The atomic values from 5p average radii give the same result (see also Figure 10). Here we

TABLE IV. Explicit Studies of Relativistic Bond-Length Contractions[u]

		R/pm[a,b]					
element	molecule	NR	R	exptl	C/pm	method	ref
H	H_2^+		106.034	105.66[c]	0.0016	P + anal.	81
		105.686877	105.684888	105.66[c]	0.00199	2D	79b
	H_2	73.354	73.352	74.152[d]	0.0017[e]	DF-LCAO	315
Li	LiH	160.89	160.87	159.41	0.016	DF-LCAO	88c
C	CH_4		108.3	108.6	0.010	P-HF	261
	$C(CH_3)_4$		154.0	153.9	0.0040	P-HF	261
Al	AlH	178.51	178.42	164.6	0.08	DF-OCE	113a
Si	SiH_4		157.2	148.1	0.1	DF-OCE	112a
			148.2		0.066	P-HF	261
	$Si(CH_3)_4$		190.2	187.5	0.066	P-HF	261
Cl	HCl	126.741	126.923	127.46	−0.18	DF-LCAO	99e
Cr	CrH_6	168.9	168.3	(167.5–172)[q]	0.6	DF-OCE	113d
Fe	$Fe(C_5H_5)_2$	174	173	166	0.7	P-CI	266
Ni	$NiH(X^2\Delta)$		148.3	146.4	2.6	P-CI(SD)	263
			150.6		1.1	P-CPF	263
	$Ni(CO)_4$	192.1	189.4	182.5	2.6	P-HF	264
Cu	CuH	150.3	148.8	146.3	1.5	DF-OCE	112b, 68
		151	150		1	P-HFS	148g
		149.7	146.9		2.8	P-CI(SD)	263
		149.4	146.8		2.6	P-CPF	263
		154	151		3	PP-HF	246a
	$CuO(X^2\Pi)$	174.9	172.1	172.4	2.8	P-CPF	216a
	$CuO(A^2\Sigma)$	167.2	164.9		2.3	P-CPF	216a
	$CuS(X^2\Pi)$	209.0	204.5	205.1	4.5	P-CPF	216a
	$CuS(A^2\Sigma)$	305.0	199.4		5.6	P-CPF	216a
	CuCl	209	209	205.1	<1	P-HFS	148g
	Cu_2	226	224	222.0	2	P-HFS	148g
		242	237		4.8	P-HF	267b
		243	240		3	PP-HF	232b
		231	225		6	PP-CI	232b
		227	222		5	PP-HF	246a
		230.8	227.1		3.7	P-CI(SD)	269
		228.0	224.3		3.7	P-CPF	269
		244	239		5	P-HF	270a
		231	227		4	P-CI(SD)	270a
		227	223		4	P-CPF	270a
		228.8	224.9		3.8	P-CPF	216b
	Cu_3	235.6	232.6		3.0	P-CPF	216b
Zn	ZnH^+	168.4	167.0	151.4	1.4	DF-OCE	68
		158	158		<1	P-HFS	148g
	ZnH	158.2	156.5	159.5	1.6	P-CI(SD)	263
		160.4	159.0		1.4	P-CPF	263
	ZnH_2[g]	159.2	157.7		1.5	DF-OCE	68
	ZnO	171	170		1	P-CI	178d
	ZnS	206	205		1	P-CI	178d
	$ZnCl_2$	210	210	206	<1	P-HFS	148g
	Zn_2^{2+}	242	240		2	P-HFS	148g
Ga	GaH	173.4	172.2	166.3	1.22	DF-OCE	68, 113a
Ge	GeH	158.66	158.42	158.80	0.24	P-HF	270b
		157.39	157.12		0.27	P-CI(SD)	270b
		159.06	158.85		0.21	P-CPF	270b
	GeH_4	159.6	158.6	152.7	1.0	DF-OCE	112a, 68
			152.1		0.70	P-HF	261
		156.8	156.2		0.7 (2)	DF-LCAO	92
	$Ge(CH_3)_4$		197.0	198	0.51	DF-LCAO	92
Br	HBr^+	142.6	142.4	144.8	0.2[n]	PP-HF	241d
	HBr	139.5	138.9	141.4	0.6	PP-HF	241c,d
	Br_2^+	219.3	218.8		0.5	PP-HF	241c
	Br_2	230.2	229.8	228.1	0.4	PP-HF	241b
Y	$YH(X^1\Sigma)$	192.9	193.7	192.2[s]	−0.79	P-CPF	216c
	$YH(^3\Delta)$	200.5	200.8		−0.26	P-CPF	216c
Zr	ZrH_4	190.9	191.3		−0.4	DF-OCE	113b
		188	187		+1	P-HFS	69
	$ZrCl_4$	240	238	232	2	P-HFS	69
Mo	MoH_6	186.6	185.0	(170–180)[q]	1.6	DF-OCE	113d
Ag	AgH	168.4	164.3	161.8	4.2	DF-OCE	112b, 68
		171	161		10	P-HFS	148g
		177.4	169.7		7.7	DF-LCAO	87a
		170.2			8.4	NR-CI vs exptl	307
		176.9	171.4		5.5	PP-HF	212
		176.3	169.4		6.9	P-HF	267a
		180	174		6.3	PP-HF	246a
		178	169		9	PP-HF	200e
		176	170		6	PP-HF	237

TABLE IV (Continued)

		R/pm[a,b]					
element	molecule	NR	R	exptl	C/pm	method	ref
		177.3	171.2		6.1	PP–HF	183
		176.2	169.7		6.5	H_+ HF	312b
		169.7	162.1		7.6	H_+ CI	312b
		169.9	162.8		7.1	P–CPF	216c
			163			PP–MP4	220b
	$AgH(A^1\Sigma)$	171.1	160.7	166.5	10.4	H_+ CI	312b
	$AgCH_3$	210[o]	202[o]		8[o]	P–HFS	140d
	$AgO(X^2\Pi)$	215	210	200.3	5	PP–HF	200e
			204			PP–MP4	220b
	$AgO(A'^2\Sigma)$	214	210		4	PP–HF	200e
			200			PP–MP4	220b
	AgCl	242	233	228.1	9	P–HFS	148g
	Ag_2	289	276	248.2[j]	13	PP–2CSCF	177a
		273	262		11	PP–CI	177a
		267	252		15	P–HFS	148g
		280.1	273.1		7	PP–HF	212
					11	PP–HF	246a
			252			PP–MP4	220b
Cd	CdH^+	186.5	182.5	166.4	4.0	DF–OCE	68
		178	174		4	P–HFS	148g
	CdH_2[g]	177.5	173.2		4.2	DF–OCE	68
	$CdCl_2$	230	228	221	2	P–HFS	148g
	Cd_2^{2+}	284	273		11	P–HFS	148g
In	InH	193.2	189.2	183.7	4.0	DF–OCE	113a, 68
		185.4	185.2		0.2[n]	PP–HF	232a
	InH_3	176.2	173.9		2.3	PP–HF	232a
Sn	SnH_2	178.7	177.5		1.2	PP–HF	232a
	SnH_4	180.4	177.2	170.1	3.2	DF–OCE	68, 112a
		173.2	171.5		1.7	PP–HF	232a
			170.5		2.1	P–HF	261
		173.6	171.7		1.9	PP–HF	193a
	$SnH_4^+(X^2A_1, C_{2v})$	185.4	182.6		2.8	PP–HF	193a
	$Sn(CH_3)_4$	215.0	214.3		1.8	P–HF	261
I	HI^+	162.9	162.1	162	0.8[n]	PP–HF	241d
	HI	160.6	159.6	160.9	1.0[n]	PP–HF	241b
	I_2^+	259.4	258.0		1.4[n]	PP–HF	241c
	I_2		273.6	266.6	2[n]	PP–HF	202
		270.2	268.9		1.3[n]	PP–HF	241b
		270.2	268.9		1.3[n]	PP–HF	241b
Xe	XeF_2		197.8	197.7	0.3[n]	PP–HF	202
	Xe_2	452[o]	434[n,o]		18[n,o]	PP–EN	173a
	Xe_2^+	324	319		5	PP–HF	188d
Cs	CsH	262	260	249.4	3	P–HFS	69
		267	265		2.6	PP–GVB	217f
		265	262		2.6	PP–CI(2 elec)	217f
		259	256		3.7	PP–CI(10 elec)	217f
	CsCl	298	296	290.6	2	P–HFS	148g
	Cs_2	520	517	447	3	P–HFS	148g
Ba	BaH^+	226.2	227.2		–1.0	DF–OCE	68
		225	224		+2	P–HFS	69
	BaH_2[g]	232.8	232.7		0.1	DF–OCE	68
La	$LaH(^1\Sigma)$	221.0	222.2	210.1	–1.2	DF–OCE	114
Ce	CeH_4	200.1	202.4		–2.3	DF–OCE[h]	113d
		208.2	209.8		–1.5	DF–OCE[i]	113d
Yb	YbH^+	205.6	201.7		3.9	DF–OCE	68
	YbH_2[g]	214.6	208.5		6.1	DF–OCE	68
Lu	LuH	201.9	201.3	191.2	0.6	DF–OCE	114
Hf	HfH_4	191.9	190.8		1.1	DF–OCE	113b
		190	185		4	P–HFS	69
	$HfCl_4$	243	238	233	5	P–HFS	69
W	WH_6	190.2	184.8	(186–189)[q]	5.4	DF–OCE	113d
	W_2H_6(W–W)	236	231	(226–229)[l]	5	P–HFS	148a
	W_2	207	203		4	P–NLDF	148i
Pt	$PtH(X^2\Delta)$	172.3	146.2	152.8	26.1	PP–HF	177i
		176.0	147.0		29.0	PP–2CSCF	177i
	$PtH(^2\Sigma)$	155.7	144.7	153.6	11.0	PP–HF	177i
		151.6	145.5		6.1	PP–2CSCF	177i
Au	AuH	174.7	162.2	152.4	12.5	DF–OCE	112b, 68
		176.3	150.8		25.5	PP–HF	200i
		182.0	151.4		30.6	PP–GVB	200i
		180.7	152.2		28.5	PP–CI	200i
		178	155		23	P–HFS	148f,g
		174.7	164		11	P–DF–OCE	115
		180	164		16	DF–LCAO	87a
		175.3			22.9	NR–CI vs exptl	307

TABLE IV (Continued)

element	molecule	R/pm[a,b] NR	R	exptl	C/pm	method	ref
		182	159		23	PP-HF	237
		180.7	156.7		24	PP-HF	183
		189.4	176.0		13.4	PP-HF	241c
		181.6	157.8		23.8	hybrid-DF	119b
		194.7	166.8		27.9	hybrid-CI	119b
	$AuCH_3$	220^{o}	202^{o}		18^{o}	P-HFS	140d
	AuCl	244.7	228.3		16.4	PP-GVB	200i
		244	231		13	P-HFS	148f,g
	AuCs	400	353		47	P-HFS	148g
	Au_2	283	248	247.2	35	PP-HF	219
		290	244		46	P-HFS	148f,g
		301	258		43	PP-HF	188d
Hg	HgH^+	193.1	180.8	159.4	12.3	DF-OCE	68
		188	164		24	P-HFS	148g
		185.7	168.5		17.2	PP-HF	241c
	HgH	195.6	185.5	174.0	10.1	PP-HF	241c
	$HgH_2{}^{g}$	184.1	170.8		13.3	DF-OCE	68
		185.8	172.0		1.8	PP-HF	241c
	$Hg(CH_3)_2$	216^{o}	203^{o}	209	13^{o}	P-HFS	142b
	$HgCl_2$	241	229	225^{m}	12	PP-HF	211i
		245	236		9	P-HFS	148g
	$Hg_2{}^+$	361	315		46	QR-MS	136
		324.2	295.7		28.5	PP-HF	241c
	$Hg_2{}^{2+}$	312	263	$250\ (1)^{k}$	49	P-HFS	148g
		281	253		28	PP-HF	233c
		282	254		28	$PP-CI^{t}$	233c
Tl	TlH	200.6	186.7	186.9	13.9	DF-OCE	113a, 68
		194	184		10	PP-HF	218
		195.2	190.2		5.0^{n}	PP-HF	232a
		200.6	188		13	P-DF-OCE	115
		192.5	187.9		4.6^{n}	PP-HF	241a
	$TlH^{+\,p}$	187.7	334.7		-147	PP-HF	241a
			253.1			PP-CI(SD)	241a
	TlH_3	184.4	173.3		11.1^{n}	PP-HF	232a
		183.7	173.9		9.8^{n}	PP-HF	241a
	Tl_2	$312^{n,o}$	376^{o}		$-64^{o,r}$	PP-CI	188g
Pb	PbH^+	183.4	179.2		4.2	PP-HF	241c
	PbH	185.7	181.8		3.9	PP-HF	241c
	PbH_2	187.3	183.7		3.6	PP-HF	232a
		185.3	181.1		4.2	PP-HF	241c
	PbH_4	189.0	178.2	$(175.4)^{f}$	10.7	DF-OCE	68, 112a
		182.7	174.3		8.4	PP	232a
			170.3		10	P-HF	261
		180.6	173.2		7.4	PP-HF	241c
	$Pb(CH_3)_4$		224.7	223.8	4.5	P-HF	261
Ra	RaH^+	239.0	239.7		-0.7	DF-OCE	69

[a] Adiabatic, potential energy minima. [b] Using 1 au = 52.9177 pm. [c] For $^3H_2{}^+$. [d] For $^2H_2$. [e] Scaling the c = 5 au result by $(5/137.0)^2$. [f] Deduced in ref 112a from experimental geometries of PbH, SnH, and SnH_4. [g] Assumed linear. [h] With f-type symmetry functions. [i] Without f-type symmetry functions. [j] From ref 318. [k] Typical value for crystals.[319] [l] Typical values for W_2L_6 compounds; see ref 148a. [m] From ref 317b. [n] A quasi-relativistic calculation. No spin–orbit splitting. [o] Estimated from the published figure. [p] This molecule dissociates to $Tl^+(6s^2)$ + H. [q] Typical M–H distances in organometallic compounds.[113d] [r] Spin–orbit contribution only. [s] Reference 216d. [t] Intravalence correlation only. [u] R_{NR} and R_R are the nonrelativistic and relativistic bond lengths, respectively, and C is the difference (39). The data are organized according to (1) the heavier atom, (2) the lighter atom in the bond, and (3) the year. Unless otherwise specified, the electronic ground state is considered and the experimental data are taken from ref 317 or from the theoretical reference given. For calculations with several basis sets, the largest one is chosen. The labels for the methods are as follows: Anal., exact analytical solution; CI, configuration interaction; CPF, coupled-pair function; DF, dirac-Fock; EN, Epstein–Nesbet; GVB, generalized valence bond; HF, Hartree–Fock; HFS, Hartree–Fock–Slater; H_+, "no-pair" approximation; MP4, fourth-order Møller–Plesset; MS, multiple scattering; NLDF, nonlocal density functional; OCE, one-center expansion; P, perturbative; PP, pseudopotential; QR, quasi-relativistic; SD, singles and doubles; 2CSCF, two-configuration self-consistent field; 2D, two-dimensional, fully numerical.

speak of the lanthanoid contraction of the ionic or covalent radii of the lanthanoids themselves. What happens with the 6s or 6p valence shells of the subsequent elements is a different story (see Figures 2 and 4). Their "lanthanoid contractions" and relativistic effects are comparable.

The corresponding actinoid contraction is about 30 pm. The f^{14} Ln and An are roughly of the same size (within 2 pm or so) while the f^0 An are some 10 pm larger than the f^0 Ln. Experimentally,[329] the ionic radius of No^{II} is close to that of Yb^{II}. For a further discussion of the Ln and An ionic radii, see ref 330.

Transition Elements. The experimental single-bond radii for a 4d element and the corresponding 5d element are closely similar. The calculations in Table IV (the model systems MoH_6 versus WH_6,[113d] $ZrCl_4$ versus $HfCl_4$[69]) suggest that the larger relativistic contraction of the 5d element (about 5 pm) would be just of the right size to accomplish this. For the 4d hexafluorides of Ru, Rh, and Pd, M–F is 187 pm while for the 5d hexafluorides of Os, Ir, and Pt, M–F is 183 pm.[331c]

A particularly interesting comparison between Pd and Pt is provided by $M(CH_3)_2(PR_3)_2$ (experimental: PR_3

TABLE V. Relativistic Contractions of Single-Bond Covalent Radii, r_{cov}, and the Corresponding Coefficients, c_Z (48) (the Data Are Chosen from Table IV)

group	element	contraction/pm	c_Z
hydrogen	H	0.0010	0.0010
1	$_3$Li	0.016	0.0018
	$_{55}$Cs	3	0.0010
6	$_{24}$Cr	0.6	0.0010
	$_{42}$Mo	1.6	0.00091
	$_{74}$W	5.4	0.00099
			av 0.00097 (5)
10	$_{28}$Ni	2.8	0.0036
	$_{78}$Pt	26	0.0043
11	$_{29}$Cu	2.0	0.0024
	$_{47}$Ag	8	0.0036
	$_{79}$Au	23	0.0037
			av 0.0032 (7)
12	$_{30}$Zn	1.4	0.0016
	$_{48}$Cd	4	0.0017
	$_{80}$Hg	18	0.0028
			av 0.0020 (7)
13	$_{13}$Al	0.08	0.00047
	$_{31}$Ga	1.22	0.0013
	$_{49}$In	4.0	0.0017
	$_{81}$Tl	13	0.0020
			av 0.0014 (7)
14	$_6$C	0.010	0.00028
	$_{14}$Si	0.066	0.00034
	$_{32}$Ge	0.7	0.00068
	$_{50}$Sn	2	0.0008
	$_{82}$Pb	10	0.0015
17	$_{17}$Cl	−0.13	−0.0006
	$_{35}$Br	0.4	0.0003
	$_{53}$I	1	0.0004

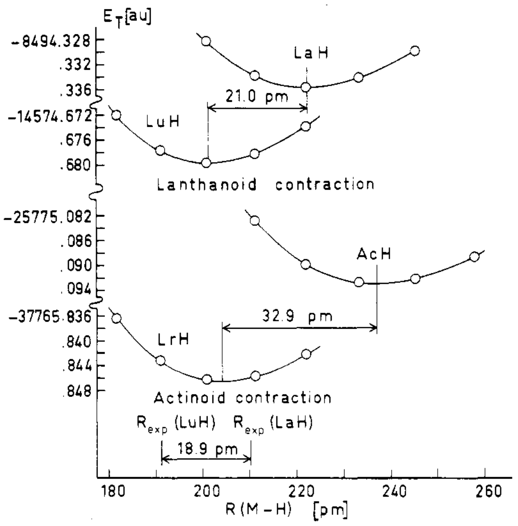


Figure 10. Calculated (DF-OCE) potential energy curves for $^1\Sigma$ states of LaH, LuH, AcH, and LrH. (Reproduced with permission from ref 114.)

= $P(C_6H_5)_2CH_3$; theoretical: $PR_3 = PH_3$).[253] As seen from Table VIII, for the M–C bond, Pt–C is 3 pm longer than Pd–C; for the M–P bond, Pt–P is 4 pm shorter than Pd–P. Theoretical pseudopotential calculations reproduced this trend.[253] (No nonrelativistic reference calculation was done.) For the linear complexes $M(PH_3)_2$, the theoretical M–P were 241 and 232 pm for Pd and Pt, respectively. Thus the relativistic pseudopotentials (cf. section III.C) are able to explain why Pt is "softer" than Pd.[253]

The average M–Cl distances in $NbCl_5$ and $TaCl_5$ were closely similar,[331a] 228.0 (3) and 228.4 (2) pm, respectively. It is not obvious why the (M–Cl(ax))–(M–Cl(eq)) difference is 9.7 (1.0) and 14.2 (7) pm, respectively. (See also Table IX for data on the pentafluorides.)

For WCl_4, the analogous (W–Cl(ax))–(W–Cl(eq)) difference is 229.5 (6) − 220.2 (6) = 9.5 pm.[331d]

If the "kinetic energy" argument still is the dominant one,[148a] it is logical that multiple metal–metal bonds, with a larger d character and smaller overlap with core s orbitals than in the single bonds with ligands, would remain longer in the 5d–5d case than in the 4d–4d case. As an example, in the compounds $(M_2(O_2CCF_3)_4{\cdot}2PR_3)$ (M = Mo, W), Mo–Mo and W–W are 210 and 222 pm, respectively, while Mo–P and W–P are closely similar, 251 pm.[331b] Ziegler[148a] indeed calculates for the triple W–W bond in W_2H_6 a contraction of only 5 pm, or 2.5 pm per atom.

In a "MO^{3+}" unit (i.e., in $MO(SCH_2CH_2S)_2^-$), Mo–O is slightly longer than W–O: the M–O are 167.8 (5) and 164.1 (10) pm, respectively.[331k]

Not enough structural data could be found on transition-metal cluster compounds[331e-g,l-n] to see trends between the 4d and 5d metal–metal bonds. In the particular case of $(C_5H_5)M^{IV}(\mu\text{-}H_2)(C_5H_4)Ir^{III}H(PMePh_2)_2^+$ the hydrogen-bridged M–Ir (M = Mo, W) were 264.1 (1) and 270.6 (1) pm, respectively.[331j]. The Au_n clusters have a unique stability; the valence AOs are predominantly 6s (for recent evidence on 5d–6s hybridization, see ref 124e,f,i).

In the bonds to the η^5 rings in $M(C_5(CH_3)_5)_2$, Ru and Os are closely similar; the average M–C are 217 (1) and 218 (1) pm, respectively. For the unmethylated cp, (C_5H_5), both distances are 219 (1) pm.[331i]

For a summary of 4d and 5d bond lengths, see Table IX.

B. Bond Angles

Few data (using rather approximative methods) are available on relativistic effects on bond angles in molecules (see Table X) and only small effects are found.

C. Catalysis and Reaction Pathways

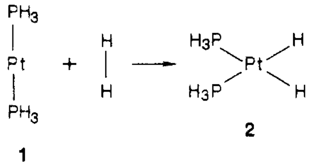
Spin-orbit effects may considerably influence the reaction cross-section between an atom and a molecule for systems as light as F + H_2.[332c] As another recent example, the chemiluminescent reaction cross-section between Sr or Ba in a ^3P_J state and the halogen-containing molecules X_2 or CH_2X_2, X = Cl, Br, and I, strongly depends on J.[332] Many other examples exist. A third example on gas-phase reactions is the dependence of the reaction

$$Kr^+(^2P_J) + H_2 = KrH^+ + H \tag{49}$$

on J.[333] For a review, see ref 332d.

The first example from organic chemistry seems to be the rearrangement of the 1,3-perinaphthadiyl biradical to phenalene. This reaction proceeds below 100 K at a temperature-independent rate, attributed by Fisher and Michl[334] to quantum mechanical tunneling from the triplet reactant to the singlet product. Both external and internal heavy-atom effects on the rate constant were seen. Without relativistic effects this reaction would not exist. Evidently, the same is true for other intersystem crossings.

Other Effects. As discussed in Table II, relativistic effects are already large enough to change electron configurations of the 5d elements. A notable case is the group 10 metals Pd ($4d^{10}$) and Pt ($6s^15d^9$), whose differences in homogeneous catalysis seem to arise from this very reason.[61,62] Low and Goddard[61] considered various oxidative addition and reductive elimination reactions, such as


(50)

They found 1 to be near a Pt $5d^{10}$ configuration while 2 corresponds to a Pt $6s^15d^9$ configuration. The metal charges were comparable (despite "oxidative addition") but the configurations were different. In the beginning of the reaction, H_2 functions as a Lewis base and Pt($6s^0$) as a Lewis acid. The barrier is low (2.34 kcal/mol). Pd favors the d^{10} configuration and therefore forms less stable complexes **2**, thus disfavoring the oxidative addition (50). No hydrogen addition to PdL_2 has, in fact, been observed. Summarizing, reductive elimination is exothermic from Pd complexes (since Pd prefers d^{10}) and endothermic from Pt complexes (since Pt prefers s^1d^9),[61c] the enthalpy difference between the two metals (for the same ligands) being always close to the atomic one of 32 (4) kcal/mol. Omitting relativistic effects for Pd would introduce a further error of 15 kcal/mol. For a review on the reactivity of Pd compounds, see ref 335.

The role of relativistic effects in the reaction mechanisms of anticancer compounds such as "*cis*-platinum", $PtCl_2(NH_3)_2$, could be expected to be equally important.[177g,291,295c,336] Zuloaga and Arratia-Perez[124j] find, in a DS-MS Xα scheme, that also the Pt 6p AOs are important. Louwen et al.[146b] find for *trans*-$MCl_2(NH_3)_2$ (M = Pd, Pt) only minor relativistic effects on the orbital energies, but much stronger Pt 5d bonds than Pd 4d bonds.

Summarizing, the study of relativistic effects in catalysis is only in its infancy. Other cases where important effects may occur are the use of Bi(V) compounds as mild oxidation reagents (e.g., $(Ph_3BiCl)_2O$[337a]) or phenylation agents (e.g., $BiPh_5$[337b]) or the use of bismuth molybdates in heterogeneous catalysis. McGlynn et al.[361c] suggest that the "formerly important" role of lead tetraethyl "antiknocks" would be an example of a heavy-atom spin–orbit effect.[427]

D. Solids

Relativistic band-structure calculations on solids are numerous; for reviews, see, e.g., ref 43 and 338–340. Rather few investigations seem to be specifically concerned with relativistic effects on crystal structures or lattice parameters.

Glötzel and McMahan[341] considered relativistic effects on the isostructural ("6s-to-5d bonding", fcc-to-fcc) phase transition of Cs. Christiansen[339] analyzed the relativistic contraction of the lattice parameters of gold (5.7% or 23 pm. The corresponding change of the nearest-neighbor distance, $a_0/2^{1/2}$, is 16 pm, about $^1/_3$ of that in Au_2; see Table IV). The spin–orbit effects are found to increase a_0 of Au by 5 pm, from 400 to 405 pm (exptl, 406 pm).[342] The final theoretical lattice parameter, a_0, is 0.7% below experiment. (The optical properties of gold will be discussed in section IV.)

Xe is expected to show an insulator–metal transition at high pressures. Relativistic effects lower the calculated transition pressure from 1.1 to 0.38–0.40 Mbar.[342]

For metallic lead Christensen et al.[343a] find a nonrelativistic diamond structure. The "relativistic dehybridization", isolating the $6s^2$ inert pair, gives the observed fcc structure for Pb as suggested earlier.[343b] Spin–orbit effects were found to increase the fcc-to-hcp transition pressure by about 100 kbar.

Lohr[305] has recently explained, at the REX (tight binding) level, the simple-cubic (sc) structure of polonium as a spin–orbit effect, leading to a filled $6p_{1/2}$ band and a half-filled $6p_{3/2}$ band with weaker directional properties than in tellurium. Te exhibits a helical structure. Similarly, while CdTe, HgTe, and CdPo have the ZnS structure, HgPo has a NaCl structure, again indicating a preference for octahedral hybridization.[382]

Also the neighboring elements Sb and Bi have high-pressure "sc" modifications.[350d] Even the normal Bi structure (three neighbors at 307 pm, three at 353 pm) could be viewed as a distorted cubic one.[350e]

Spin–orbit effects on the lattice parameters of the actinoids Ac to Am were considered by Brooks.[344]

Treglia and Ducastelle[408] asked whether the ordering in platinum–nickel alloys is induced by spin–orbit interactions.

Kaveh and Mott[416] found that spin–orbit interactions cause a low-temperature metal–insulator transition in doped silicon.

An interesting case is the ionic crystals RbAu and CsAu, where explicit calculations show that the ionic Cs^+Au^- structure is caused by relativistic effects; without them CsAu would be a metallic alloy.[345a-d] Other examples of metal–nonmetal transitions occur in Mg–Bi (about Mg_3Bi_2) and Cs–Sb (about Cs_3Sb).[345e]

Ionic Models. An old line, going back to Löwdin,[346] in the theory of the cohesive properties of ionic crystals is the treatment starting from suitable wave functions for the individual ions. Relativistic generalizations exist now,[153-157] with applications to heavy systems such as AgF or PbF_2.[154] The calculated relativistic cohesive energies and structures are reasonable; no nonrelativistic reference calculations are reported.[428]

Semiempirical Calculations. The structures of red and yellow PbO have been discussed at the extended Hückel level.[304a,347] The parameters used include "scalar relativity", in particular the $6s^2$ inert-pair effect. In this case Hoffmann and Trinquier[304a] made also an attempt to isolate the relativistic contributions using NR reference parameters. The band structure changed by several eV but the nature of bonding remained unchanged.[304a]

The structures of alloys and their interpretation using atomic radii were recently reviewed by Simon.[350f] One interesting case is NaTl, the Tl forming a diamond lattice with interstitial Na^+ ions.[407]

The occurrence of the Au_3Tl eutectic[350g] at 131 °C (T_m(Au) = 1064, T_m(Tl) = 303 °C) is interesting. Could it contain Au_3Tl "trihalides"?

E. The Inert-Pair Effect

Sidgwick[42a] coined the term "inert pair" for the tendency of the $6s^2$ electron pair to remain formally unoxidized in compounds of Tl(I), Pb(II), Bi(III), etc.

As mentioned in the Introduction, this tendency was

TABLE VI. Covalent Radii[ee] (pm) for Discrete Hydride or Halide Molecules and Pauling Radii for Covalent Crystals

group	element	CN	r_{cov}(present)	r_{cov}(Pauling)[a]	group	element	CN	r_{cov}(present)	r_{cov}(Pauling)[a]
1^d	Li	1	101	123	$Ln^{i,j}$	Yb(II)[d]	1, 2	153	
	Na		131	157		Sc(III)	3	129	
	K		166	203		Y(III)	3	145	
	Rb		179	216		La(III)	3	160	
	Cs		191	235[c]		Ce(III)	3	159	
2^d	Be	2	78	89		Pr(III)	3	157	
	Mg		117	136		Nd(III)	3	156	
	Ca		152	174		Pm(III)	3	154	
	Sr		169	191		Sm(III)	3	153	
	Ba		185	198		Eu(III)	3	151	
	Ra		195			Gd(III)	3	150	
4^d	Ti(IV)	4	114	132		Tb(III)	3	149	
	Zr		133	145		Dy(III)	3	148	
	Hf		133	144		Ho(III)	3	147	
	104		136			Er(III)	3	146	
6^d	Cr(VI)	6	110	118		Tm(III)	3	145	
	Mo(VI)		127	130		Yb(III)	3	144	
	W(VI)		127	130		Lu(III)	3	142	
	106(VI)		133		An	Th(IV)[d,m]	4	158[e]	165
$11^{d,e}$	Cu(I)	1, 2	106	117		U(IV)[i,k,n]	4	153	
	Ag(I)		128	134		U(VI)[i,l]	6	137	
	Au(I)		127	134		No(II)[d]	2	152	
$12^{d,e}$	Zn	2	106	125, 131[b]	ligands[u]	H[d]	1	58	
	Cd		122	141, 148[b]		$C(sp^3)$[d]	4	97	
	Hg		126	144, 148[b]		η^5-$C_5H_5^-$(M–C)[i,o]		125	
						η^3-BH_4^-(M–H_b)[d,s]		74	
						η^3-BH_4^-(M–B)[i,t]		98	

[a] Reference 321. [b] Reference 322. [c] Given as 253 in ref 321. [d] References 68 and 113d. [e] These radii hold for the halides. For groups 11 and 12 the appropriate hydrogen radius is closer to the "covalent" value of 30 pm than to the "hydridic" one of 58 pm, indicating greater covalency, especially for Ag an au. Indeed, the calculated charges for Au are $Au^{+0.02}H^{-0.02}$.[183,200i] Similarly, the experimental[f] Au–C of 203.4 (12) pm for $MeAuPMe_3$ corresponds to an r_C of 76 pm, close to the Pauling value of 77 pm. Note that (OC)AuCl has a much shorter Au–C of 193 (2) pm but an Au–Cl of 226.1 (6) pm, in agreement with our radii.[g] The cyanide would be still smaller than the carbonyl; the Au–C of Ph_3AuCN is only 185 (4) pm.[h] [f] Haaland, A.; Hougen, J.; Volden, H. V.; Puddephatt, R. J. *J. Organomet. Chem.* **1987**, *325*, 311. [g] Jones, P. G. *Z. Naturforsch. B* **1982**, *37b*, 823. [h] Bellon, P. L.; Manassero, M.; Sansoni, M. *Ric. Sci.* **1969**, *39*, 173 (as quoted by Jones[g]). [i] Present work. [j] Based on the gaseous lanthanoid trihalide data.[326] [k] Based on the data for MX_4 (M = Th, U, X = Cl, Br) by: Ezhov, Yu, S.; Akishin, P. A.; Rambidi, N. G. *Zh. Strukt. Khim.* **1969**, *10* (5), 763. [l] Based on the data for UF_6 and UCl_6.[113d] [m] In the hexacoordinate $Th(CH_2Ph)_4(Me_2PCH_2CH_2PMe_2)$,[325] the Th–C(Bz) of 255 (2) pm would also be consistent with $r_{Th} = 255 - 97 = 158$ pm. [n] In the hexacoordinate U(IV) compound $U(CH_2Ph)_3Me(Me_2PCH_2CH_2PMe_2)$,[325] the U–C(Me) and U–C(Bz) are 241 (1) and 250 (3) pm, respectively, corresponding to an r_U of 144 and 153 pm, respectively. [o] Based on the M–C(η^5) distances of 258 (3) pm in $Zr(cp)_4$,[p] 238 pm in $Ti(cp)_4$,[q] and 283 pm in $Th(cp)_2(C_5H_4)_2$.[r] Agrees also with the M–C(η^5) distances for M = Sc, Ln, and U in Table III of: Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 276. [p] Rogers, R. D.; Vann Bynum, R.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238. [q] Calderon, J. L.; Cotton, F. A.; Deboer, B. G.; Takats, J. *Ibid.* **1971**, *93*, 3592. [r] Baker, E. C.; Raymond, K. N.; Marks, T. J.; Wachter, W. A. *Ibid.* **1974**, *96*, 7586. [s] The new Zr–H_b[t] agrees with this radius. [t] Data for $M(H_3BCH_3)_4$ (M = Zr, Th, U) by: Shinomoto, R.; Gamp, E.; Edelstein, N. M.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 2351. [u] In addition to these ligand radii, directly fitted to experimental M–L distances, one could deduce the following ligand radii by halving the L–L dimer bond length (just as done by Pauling for the halogens): $-OCH_3$, 73;[v] $-SCH_3$, 101;[x] -CN, 69;[y] $-NR_2$, 73.[aa] [v] From HOOH, Wells,[350c] p 501. Fits perfectly the U–O of 210 pm in $U(OMe)_6$.[w] [w] Miller, S. S.; Day, V. W.; Marks, T. J., to be published. [x] From several RSSR compounds, Wells,[350c] p 728. [y] From $(CN)_2$, Wells,[350c] p 928. This cyanide radius would predict for $Hg(CN)_2$ a Hg–C of 195 pm (exptl 198.6 pm, Wells, p 941). While the cyanide–mercury bond is essentially a single bond, the cyanide–gold bond will also contain 5d-to-π^* back-bonding and is therefore shorter than predicted. [z] Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *Chem. Commun.* **1970**, 30. [aa] From N_2H_4 or $N_2(SiH_3)_4$, Wells,[350c] p 803. Predicts for W–N 200 pm; exptl in $W(NMe_2)_6$ 203.2 (2.5) pm.[bb] Predicts for M–N (M = Zn, Cd, Hg) 179, 195, and 199 pm; exptl in $M(N(SiMe_3)_2)_2$ 182 (1), 203 (2), and 201 (2) pm, respectively.[cc] Predicts for Be–N 151 pm; exptl in $Be(NMe_2)_2$ 157 pm.[dd] [bb] See: Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259 (p 309). [cc] Alyea, E. C.; Fisher, K. J.; Fjeldberg, T. *J. Mol. Struct.* **1985**, *130*, 263. [dd] See Bradley,[bb] p 314. [ee] The values are tentative. These radii are consistent with Pauling's $r_F = 64$, $r_{Cl} = 99$, $r_{Br} = 114$, and $r_I = 133$ pm and lead to the ligand radii at the end of the table. For the CO group, the average r_{CO} from $M(CO)_6$, M = Cr to W, would be 80 pm (data from Wells,[350c] p 959). Finally, as a counterexample, we note that the effective radius of the $-PR_3$ group seems to decrease by 15 pm from M = W to M = Pt in the series $M^{IV}Cl_4(PR_3)_2$.[z] Thus it would be more difficult to find a good covalent radius for phosphines of these metals. **Notes added in proof**. The present sulfur radius[u] would be 5, 13, 17, and 20 pm, too short for bonds to certain Mo,[ff] Th,[gg] Hf,[hh] and Zr[hh] compounds, respectively. The analogous phosphorus radius for PR_2 groups, 110 pm,[ii] would likewise be 11 pm shorter than required for U–P in $(cp^*{}_2U(OMe))_2PH$.[jj] The average K–C in $(Me_3Si)C_5H_4K$ is 300 pm, the present radii predict 291 pm.[kk] The U–C in MeLi $U[OCH(CMe_3)_2]_4$ is 247 pm.[ll] The present U(IV) radius would predict 250 pm. The available lanthanoid-C(η^5) radii agree well with the predicted ones. As an example, Sm–C(η^5) in $Smcp^*{}_2cp$ are 277 and 274 for cp* and cp, respectively. Predicted 278 pm.[mm] [ff] Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227. [gg] Lin, Z. R.; Brock, C. P.; Marks, T. J. *Inorg. Chim. Acta* **1988**, *141*, 145. [hh] Shaver, A.; McCall, J. M.; Day, V. W.; Vollmer, S. *Can. J. Chem.* **1987**, *65*, 1676. [ii] Wells,[350c] p 847. [jj] Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907. [kk] Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew, Chem.* **1987**, *99*, 563. [ll] Stewart, J. L.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1846. [mm] Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292.

related to relativity in ref 43. As an illustration, we give the relativistic and nonrelativistic valence orbital energies for Sn and Pb in Figure 11.

The situation is, however, more complex if the local geometry at the heavy atom is discussed. Consider a cubic ML_6 complex such as $Pb^{II}Cl_6^{4-}$. Some of them are found to be strictly cubic (O_h) while others are distorted. These two cases are known as "stereochemically inactive" and "stereochemically active" (s^2) lone pairs.[348-353] No relativistic ab initio calculations seem to be available on the intra- and intermolecular[349] mechanisms producing this effect.

Lefebvre et al.[409] analyzed the nature of the Sb(III) $5s^2$ lone pair by combining structural, Mössbauer, band

TABLE VII. Relativistic and Nonrelativistic Calculated Values for the Lanthanoid and Actinoid Contractions

f^0 system	f^{14} system	property	contraction/pm NR	R	diff	ref
CeH_4	HfH_4	R	16.4	19.0	2.6	113d
LaH^c	LuH	R	19.1	21.0	1.9	114
La	Lu	$\langle r\rangle_{5p}{}^a$	19.6	21.3	1.7	11
La	Lu	$\langle r\rangle_{5p}{}^b$	19.6	20.7	1.1	11
ThH_4	$(104)H_4$	R		30.2		113d
UH_6	$(106)H_6$	R		29.5		113d
AcH	LrH	R		32.9		114

[a] Average. [b] $5p_{3/2}$ only. [c] $^1\Sigma$ states. Experimental contraction 18.9 pm.

TABLE VIII. Experimental and Calculated M-C and M-P Distances (pm) in *cis*-$M(CH_3)_2(PR_3)_2$[253]

bond	exptl	theor
Pt-C	212.0 (4)	206
Pd-C	209.0 (2)	202
diff	3.0 (4)	4
Pt-P	228.4 (1)	246
Pd-P	232.3 (1)	250
diff	-3.9 (1)	-4

gap, and photoemission data with semiempirical theoretical densities of states for the five compounds SbI_3, Sb_2Te_3, SbTeI, TlSbS and Tl_3SbS_3. They found that the total $5s^2$ population was close to two (the vacancy was under 0.1 electrons) in all cases. The central factor in going from an inactive pair with a large band gap to an active pair and then to an inactive pair in a semimetal was that the 5s levels rose from the bottom to the top of the valence band along the series.

Reiterating,[354] the relativistic thing is the difficulty of oxidizing Pb(II) or Bi(III). Their lone pairs are influenced by relativistic effects but are not in themselves more astonishing than the more perspicuous ones of P(III), S(IV), As(III), Se(IV), or Br(V). Furthermore, the "stereochemical activity" is a question of the time scale:[43d] the crystallographic, time-average pictures (of, e.g., NaCl-type PbS, CsCl-type TlI, Cs_2TeCl_6, or $Co(NH_3)_6BiCl_6$) may legitimately differ from those obtained from optical spectra or other short-time-scale methods.

For the $4s^2$ and $5s^2$ inert pairs, see section V.[422]

IV. Other Properties

A. Force Constants

Concomitant with a relativistic bond-length contraction, the corresponding stretching force constant shows a relativistic increase; see the references in Table IV. As an illustration, we show the existing results for the group 11 diatomics, M_2, and group 12 $M_2{}^{2+}$ in Table XI.

Already for Cu_2, the increase is about 13–20 cm^{-1} or 5–8%[270a] of the experimental value, depending on the approximation. For Ag_2, the increase is about 10 and for Au_2 or $Hg_2{}^{2+}$, roughly 50% of ω(exptl).

Now the nonrelativistic force constants of a 4d and 5d metal–ligand bond are comparable, while relativistic effects make those of the 5d one larger (comparing, e.g., Mo-H and W-H bonds[113d]).

B. Dissociation Energies

This case is more delicate: already Figure 7 shows that while all three bond lengths for Au_2, AuH, and AuCl suffer a contraction, only the first two show a relativistic increase of D_e. For the more ionic case of AuCl (Mulliken charges $Au^{+0.49}Cl^{-0.45}$ [200i]), D_e actually decreases.[148f,g,177i,200i]

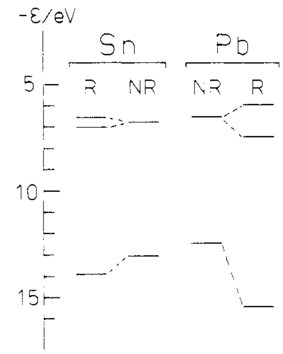


Figure 11. Relativistic (R) and nonrelativistic (NR) Hartree–Fock orbital energies[37] for tin and lead. Note the relativistic increase of the s–p gap, leading to a $6s^2$ inert pair.

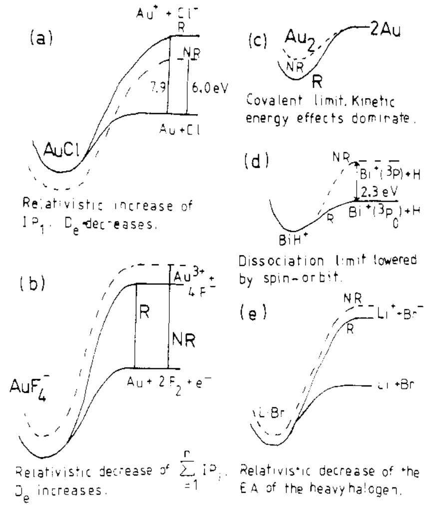


Figure 12. Various relativistic effects on the dissociation energy, D_e. (a) Ionic molecule, IP(cation) increased by relativity. (b) Ionic molecule, IP_{total}(cation) decreased by relativity. (c) Covalent limit, kinetic energy effects at R_e dominate. (d) Spin–orbit effects at the dissociation limit lower D_e. (e) Spin–orbit effects at the dissociation limit increase D_e.

The analysis is evidently that a dissociation curve has two ends, one at R_e and one at $R = \infty$, and for determining D_e, both count. In addition to the relativistic decrease of the overlap-related kinetic energy near R_e (see section II.D), one must include the relativistic change of the ionization potential for

$$Au \rightarrow Au^+ + e^- \qquad (51)$$

if the situation near R_e is closer to an ionic description. This situation is shown schematically in Figure 12a. Koopmans estimate[37] for the relativistic increase of IP_1 of Au and the corresponding decrease of D_e at the ionic limit would be 1.9 eV.

The opposite situation is expected to arise when the total ionization energy of the metal

$$\sum_{i=1}^{n} IP_i \qquad (52)$$

decreases due to relativity, a case expected for Au^{III} or Au^V compounds (Figure 12b). In the covalent case, Figure 12c, the entire relativistic increase of D_e comes

TABLE IX. Comparison of Experimental Bond Lengths (pm) with Various Ligands for Isostructural 4d and 5d Transition Element Compounds

ligand	metals	molecule	CN	*R*(4d)	*R*(5d)	diff[a]	ref
^1H	Ag, Au	MH	1	161.81	152.385	−9.42	317
	Cd, Hg	MH^+	1	166.72	159.44	−7.28	317
C(sp^3)	Pd, Pt	$MMe_2(PR_3)_2$	4	209.0 (4)	212.0 (4)	3.0 (4)	253
	Cd, Hg	MMe_2	2	211.2	208.3 (5)	−2.9	*i*
C(η^5)	Ru, Os	M(cp*)$_2$[e]	10	217 (1)	218 (1)	1 (1)	331h
	Ru, Os	M(cp)$_2$[f]	10	218.6	219 (1)	0 (1)	331i
N	Cd, Hg	$M(N(SiMe_3)_2)_2$	2	203 (2)	201 (2)	−1 (2)	*l*
≡N	Mo, W	$(RO)_3M{\equiv}N$	4	166.1 (4)	174.0 (15)	7.9 (1.5)	*b*
—O	Mo, W	$(RO)_3M{\equiv}N$		188.2 (4)	187.2 (7)	−1.0 (7)	*b*
=O	Zr, Hf	MO	1	171.16	172.307	1.15	317
	Mo, W	$MO(SCH_2CH_2S)_2^-$	5	167.8 (5)	164.1 (10)	−3.7 (1.0)	331k
	Mo, W	MOF_4	5	165.0 (7)	166.6 (7)	1.6 (7)	*j*, *k*
	Mo, W	$MOCl_4$	5	165.8 (5)	168.5 (15)	2.7	*c*
F	Zr, Hf	MF_4	4	190.2 (4)	190.9 (5)	0.7 (5)	*g*
	Nb, Ta	MF_5(ax)	5	190.5 (2)	188.6 (5)	−1.9 (5)	*p*
		MF_5(eq)	5	182.9 (1)	184.2 (3)	1.3 (3)	
		MF_5(av)		185.9	186.0		
	Mo, W	MF_6	6	184 (2)	183.3 (8)	0	*g*
		MOF_4	5	183.6 (3)	184.7 (2)	1.1 (3)	*j*, *k*
	Ru, Os	MF_6	6	187.75	183.1 (8)	−9.7 (8)	*g*, 331c
	Rh, Ir	MF_6	6	187.38	183.0 (8)	−4.4 (8)	*g*, 331c
	Pd, Pt	MF_6	6	187	182.9	−4	331c
	Ag, Au	MF	1	198.318			317
	Cd, Hg	MF_2	2	197 (2)			*g*
P	Mo, W	$M_2(O_2CR)_4{\cdot}2PR'_3$		251	251	0	331b
	Pd, Pt	$MMe_2(PR_3)_2$		232.3 (1)	228.4 (1)	−3.9 (1)	253
Cl	Zr, Hf	MCl_4	4	232 (2)	231.6 (5)	0 (2)	*g*, *m*
	Nb, Ta	MCl_5(ax)	5	233.8 (6)	236.9 (4)	3.1 (6)	331a
		MCl_5(eq)		224.1 (4)	222.7 (3)	−1.4 (4)	
		MCl_5(av)		228.0	228.4		
	Mo, W	MCl_6	6		226 (2)		*g*
		$MOCl_4$	5	227.9 (3)	228.0 (3)	0.1 (3)	*c*
		$MCl_4(C_{2v})$(ax)	4		229.5 (6)		*h*
		$MCl_4(C_{2v})$(eq)			220.2 (6)		
	Ag, Au	MCl	1	228.079	(231)[n]	3	317
	Cd, Hg	MCl_2	2	221 (2)	225.2 (5)	4 (2)	*d*, *i*
Br	Zr, Hf	MBr_4	4	246.5 (4)	245.0 (4)	−1.5 (4)	*g*
	Nb, Ta	MBr_5	5	246	245	−1	*d*
	Ag, Au	MBr	1	239.309			317
	Cd, Hg	MBr_2	2	239.4 (4)	244	7	*d*, *o*
I	Zr, Hf	MI_4	4	266.0 (5)	266.0 (5)	0.0 (5)	*g*
	Ag, Au	MI	1	254.462			317
	Cd, Hg	MI_2	2	255 (2)	261 (1)	6 (2)	*d*, *i*
M–M	Mo, W	$M_2(O_2CR)_4{\cdot}2PR'_3$		210	222	12	331b
	Ag, Au	M_2	1	248.2	247.19	−1.0	317, 318

[a] (M(5d)–X) – (M(4d)–X). [b] Chan, D. M. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S. *Inorg. Chem.* **1986**, *25*, 4170. [c] Hagen, K.; Hobson, R. J.; Holwill, C. J.; Rice, D. A. *Inorg. Chem.* **1986**, *25*, 3659. [d] Wells,[350c] p 444. [e] cp* = C_5Me_5. [f] cp = C_5H_5. [g] Krasnov, K. S. *Molecular Constants of Inorganic Compounds* (in Russian); Khimiya: Leningrad, 1979. [h] Ezhov, Yu. S.; Komarov, S. A. *Zh. Strukt. Khim.* **1984**, *25* (1), 82. [i] Landolt-Börstein *Zahlenwerte und Funktionen*, Springer: Berlin, 1976; Vol. II/6. [j] Iijima, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 373. [k] Robiette, A. G.; Hedberg, K.; Hedberg, L. *J. Mol. Struct.* **1977**, *37*, 105. [l] Alyea, E. C.; Fisher, K. J.; Fjeldberg, T. *J. Mol. Struct.* **1985**, *130*, 263. [m] Girichev, G. V.; Petrov, V. M.; Giricheva, N. I.; Utkin, A. N.; Petrova, V. N. *Zh. Strukt. Khim.* **1981**, *22* (5), 65. [n] Theoretical value, ref 148f,g. [o] Petrov, V. M.; Utkin, A. N.; Girichev, G. V.; Ivanov, A. A. *Zh. Strukt. Khim.* **1985**, *26* (2), 52. [p] Petrova, V. N.; Girichev, G. V.; Petrov, V. M.; Goncharuk, V. K. *Zh. Strukt. Khim.* **1985**, *26* (2), 56. These values include three-atom scattering.

TABLE X. Relativistic Effects on Bond Angles

		value, deg					
molecule	angle	NR	R	exptl	change/deg	method	ref
$Cu_3(X^2B_2)$	CuCuCu	65.5	64.5		−1.0	P-CPF	216b
SnH_2	HSnH	93.8	93.5		−0.3	PP-HF[a]	232a
PbH_2	HPbH	93.2	92.7		−0.5	PP-HF[a]	232a
		91.6	92.25		+0.65	PP-HF[b]	199
			91.7		+1.0	REX	320
$PbCl_2$	ClPbCl	98.6	98.15	96 (3)	−0.45	PP-HF[b]	199
H_2Po	HPoH	98.1	95.1		−3	REX[c]	293c

[a] Quasi-relativistic model, no spin–orbit effects included. [b] Spin–orbit effects only included. [c] Relativistic extended Hückel. For the other acronyms, see footnotes to Table IV. Equal relativistic and nonrelativistic bond lengths assumed.

from the kinetic energy decrease.

There also are several well-documented cases where the atomic, spin–orbit effects lower the energy of the dissociation limit, and thus D_e: BiH^+,[175h] Pb_2,[176b] PbO,[176d] PbH,[176e] or Tl_2[188g] (Figure 12d).

Finally, we have the possibility, sketched in Figure 12e, where relativistic (spin–orbit) effects *lower* the ionic limit by decreasing EA and thus increase D_e. For Br, this contribution is of the order of 0.2 eV.[37] Matcha[259] indeed finds, using perturbation theory, that the spin–

TABLE XI. Relativistic Effects on Stretching Vibration Frequencies of Group 11 Diatomics and the Isoelectronic Group 12 Ions, M_2^{2+}

species	ω/cm^{-1} NR	R	exptl	method	ref
Cu_2	268	274	265[c]	P-HFS	148g
	242	263		P-CEPA-1	270a
Zn_2^{2+}	183	187		P-HFS	148g
Ag_2	184	203	192	P-HFS	148g
	130	145		PP-HF	212
	165	186		PP-HF[d]	246a
Cd_2^{2+}	141	161	183[a]	P-HFS	148g
Au_2	93	201	191	P-HFS	148f,g
	91	138		PP-HF	219
	77	163		PP-HF	188d
Hg_2^{2+}	107	182	182[a,b]	P-HFS	148g
	115	182		PP-CI	233c

[a] Reference 355. [b] In $Hg_2(AsF_6)_2$. [c] Reference 317. [d] Includes a core–valence correlation correction.

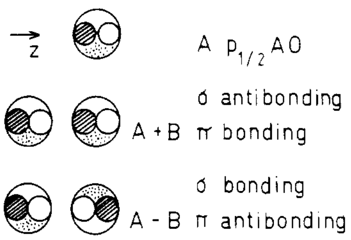


Figure 13. Bonding between two $p_{1/2}$ atomic orbitals. The charge density for this AO has a spherical symmetry, consisting of a π-like part (dotted) and a σ-like part (dashed).

orbit terms increase the D_e of LiBr by +0.30 eV. The combined mass-velocity and Darwin terms gave only +0.03 eV.[410]

We also may lower the ionic limit at R_e by increasing EA, a possible contribution to having a D_e of 1.9_5 and 3.34 eV for the ionic AgAl and AuAl, respectively. The bond lengths are 247.28 and 233.84 pm, respectively.[317] No data are available for comparing alkali-metal argentides and aurides.

A case of fundamental chemical importance is that of the mercurous ion, Hg_2^{2+}. Neisler and Pitzer[233c] have now explicitly shown that relativistic effects contribute about 1.0 eV to its D_e.

Spin-Orbit Effects near R_e. Pitzer[11,356] made in 1975 the interesting observation that the *jj*-coupled states $p_{1/2}(1/2)$ and $p_{3/2}(1/2)$ are incapable of giving good σ or π bonds. As shown in Figure 13, the bond between two $p_{1/2}$ atoms is either one-third σ bonding and simultaneouslytwo-thirds π antibonding or vice versa. Similarly, two $p_{3/2}(1/2)$ AOs are two-thirds σ bonding and one-third π antibonding or vice versa. The $p_{3/2}(3/2)$ orbitals still make a good π bond, leading to a bond order of about 1 for Bi_2.[188b] For diatomics, the spin-orbit effects at R_e thus have a tendency to weaken the bond.

The D_e of the halogen molecular ions HX^+ and X_2^+ were related to this argument in ref 294a.

The exact nature of the bonding in polyatomic, heavy main-group compounds like the Zintl anions[357a] (e.g., Pb_5^{2-}) or multiple Bi–Bi bonds with secondary ligands (e.g., $(CO)_5W_3Bi_2$[358]) is so far unknown.

In the series Sb_4, $BiSb_3$, ..., Bi_4, the dissociation energies systematically decrease from 9.04 (15) to 6.03 (8) eV.[357b]

Transition Metals. Ziegler[148a] studied the triple-bonded model compounds M_2L_6 (M = Cr, Mo, W; L = H, CH_3, Cl, NH_2, OH) using the P-HFS method. For L = H, the nonrelativistic M–M bond energies were 301, 447, and 422 kJ mol^{-1}. Relativistic effects increased the W–W bond energy to 535 kJ mol^{-1}, thus making the W–W bond the strongest. This strengthening was again obtained with perturbation theory, without the relativistic orbital changes. For other M–M bonds (M = W, Re, Ta), see ref 148i, and for the metal–ligand bonds of mononuclear complexes of Re and Ir, see ref 148j.

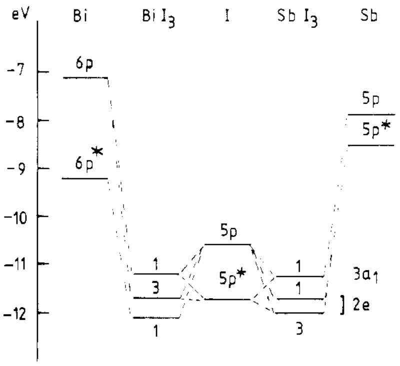


Figure 14. Calculated REX orbital energies for BiI_3 and SbI_3 from ref 144. The order for BiI_3 is dominated by Bi spin-orbit coupling while that for SbI_3 is the nonrelativistic one, split by iodine spin-orbit effects.

It has been suggested that the relativistic self-consistent, radial expansion and energetic destabilization of the 5d and 5f AOs would "activate" them for chemical bonds[10,18,19,113d,177i] (see also Figure 12b). Whether, and in which cases, this notion is true remains to be shown.

For the group 6 dimers, Ziegler[148h] finds that the stability order is changed from $Mo_2 > W_2 > Cr_2$ to $W_2 > Mo_2 > Cr_2$ by relativity.

In the $M_2(OR)_6$ compounds, the W_2^{6+} center exhibits a greater reducing power (π back-bonding) than the Mo_2^{6+} one.[254]

C. Fine-Structure Splittings

For reviews on the subject, see ref 255. The relativistic theory of zero-field splittings was discussed by Case.[125]

D. Ionization Potentials, Electron Affinities, and Photoelectron Spectra

For a concise summary on relativistic calculations of IP, EA, and PES, see Tables 9.8 and 9.9 of ref 2 and the latest references to Balasubramanian,[175f-l] Di Bella et al.,[191] Dyke et al.,[143d] Katrib et al.,[137b] Loder,[137e] Louwen et al.,[146b] Rösch et al.,[130e-h] and Snijders et al.[141]

The photoelectron spectra of bismuth trihalides were obtained by Egdell and interpreted in ref 144a by REX calculations, confirmed by perturbative Hartree–Fock–Slater (P-HFS) calculations. The central conclusion was that the hybridization of the Bi–X σ-bonding levels is fundamentally different from the (2e, $3a_1$) one of the lighter congeners EX_3 (E = N to Sb, X = F to I); see Figure 14. In the latter case the halogen atom spin–orbit splitting perturbs the lower, 2e MO. In the case of bismuth, one must start from the bismuth spin–orbit splitting of $\epsilon(6p_{3/2}) - \epsilon(6p_{1/2}) = 2.10$ eV. The upper, $6p_{3/2}$ level is then split by chemical bonding.

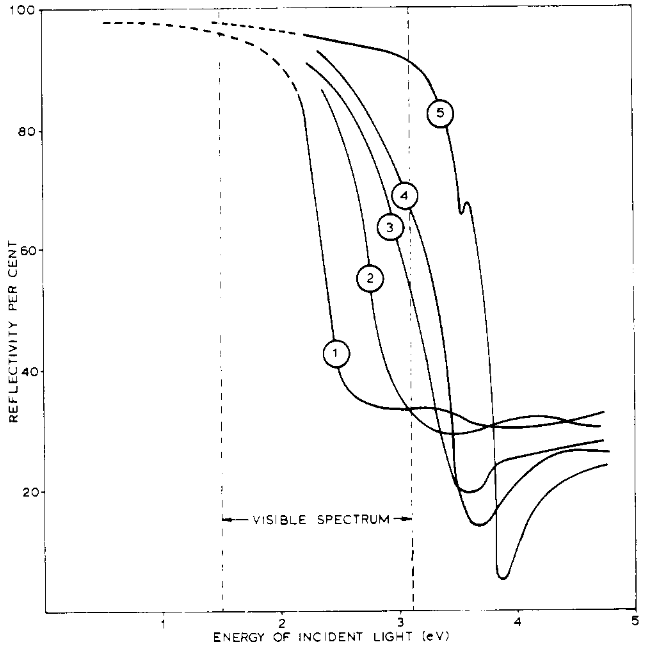


Figure 15. Experimental optical reflectivities of pure gold (curve 1), pure silver (curve 5), and their alloys. Reproduced with permission from Saeger and Rodies.[360a] Data from Fukutani and Sueoka.[360b]

Thus one could say that for the trihalides of nitrogen to antimony, relativity perturbs the chemistry while for bismuth, chemistry perturbs the relativity. Independent experiments on BiX_3 by Novak and Potts[144b] were interpreted the same way.

The photoelectron spectra of linear Hg compounds, in particular the role of spin–orbit splitting and hybridization for the 5d levels, were studied by De Kock et al.[142b]

E. Colors

Relativistic effects can be seen with the naked eye in cases where they strongly influence the color of a substance. Perhaps the most striking example is the yellow color of gold.[12,359f] The experimental reflectivities of Au, Ag, and their alloys are shown in Figure 15. The sudden onset of an absorption at $h\nu = 2.4$ eV for fine gold is assigned[359a] to a transition from the filled 5d band to the (essentially 6s) Fermi level. The calculated relativistic interband edge was 2.38 eV and its relativistic decrease was of the same order.[359a] For silver the corresponding relativistic raising of 4d and lowering of 5s are much smaller, and the analogous absorption occurs around 3.7 eV in the ultraviolet. Nonrelativistic gold would thus be white, like silver. This conclusion is confirmed by the later work on the band structure of gold.[359b–k]

Note that the transition $5d^{10}6s^1$–$5d^96s^2$ is parity-forbidden. Thus the free gold atom is actually "transparent and not yellow", although the color of the metal is due to atomic properties.

Other examples will undoubtedly be found. The thio and seleno anions of 4d and 5d transition elements are a likely case; see Table XII. In this case the (predominantly 5d) LUMO of the heavier compound will be relativistically destabilized, which increases ν_{vis} for the 5d element.[426]

A similar explanation would fit the half-wave reduction potentials of $MoCl_6$ versus WCl_6. they are systematically some 0.8 V higher for the 5d metal than for the 4d metal.[362]

TABLE XII. First Visible Absorption Band and Color of Certain 4d- and 5d-Element Thio and Seleno Anions[a]

compd	color	$\nu_{vis}(A1)/(10^3\ cm^{-1})$
Tl_3NbSe_4	deep violet	19.3
Tl_3TaSe_4	yellow-green	21.2
MoS_4^{2-}	red	21.4
WS_4^{2-}	yellow	25.5
$MoOS_2Se^{2-}$	red	24.3
WOS_2Se^{2-}	yellow	29.1

[a] Reference 361. Other examples are given in this reference.

Sakai and Miyoshi[240h] find that relativistic effects reduce the electron affinities of WF_6 and WF_6^- by 1.1 and 1.2 eV, respectively. This can be directly attributed to the relativistic destabilization of the 5d AO holding the electron removed.

For a review on the colors of post-transition-metal salts, see McGlynn et al.[361c] According to them, $AgNO_3$ is colorless but $AuNO_3$ distinctly yellow.

In addition to the colors, the intensities of fifth-row and sixth-row systems may differ drastically. In cathodic electroluminescence at oxide-covered aluminum electrodes, the intensities for Hg(II) and Pb(II) are two orders of magnitude larger than the intensities of Cd(II) and Sn(II), respectively.[412]

F. Charge Distributions and Molecular Moments

Ros et al.[147] considered the "deformation densities", due to molecular formation, of the dichlorides MCl_2 (M = Zn, Cd, Hg) and concluded that the relativistic effects, of about 0.02 e/a_0^3, would be detectable for $HgCl_2$.

The available data on relativistic effects on dipole moments are collected in Table XIII. There are relativistic changes of μ, both due to electronic reorganization at a given R and due to the relativistic change of R.

A consensus seems to exist on the relativistic change of the dipole moment of AgH and AuH, but not GeH. The AuH value is almost halved by relativity. Experimental data on AgH and AuH would be most interesting. It also is remarkable that the relativistic change of the dipole moment should be as large as 0.98, −9.9, and −27% for HCl, HBr, and HI, respectively. Accurate experimental values exist for these three dipole moments. For HI, it is clearly necessary to include relativity. For correlated pseudopotential calculations including spin–orbit effects, see ref 187b (HBr) and 187c (HI).

The relativistic decrease of the LiH dipole moment, −0.0004 D, would remove about half of the remaining deviation from experiment, or +0.0010 (2) D.

G. Magnetic Resonance Parameters

Spin–Spin Coupling. The nonrelativistic theory of Ramsey[363] is based on a nonrelativistic hyperfine Hamiltonian and LS-coupled electronic wave functions. Its relativistic counterpart[364] uses the relativistic hyperfine Hamiltonian

$$H_{hfs} = ec\boldsymbol{\alpha}\cdot\mathbf{A}_N \qquad (53)$$

and relativistic, jj-coupled molecular orbitals. One qualitatively new prediction was a new coupling term, $\mathbf{J}_{sp}$, involving s AOs on one nucleus and p AOs on an-

TABLE XIII. Relativistic Effects on Dipole Moments (in Debye, 1 D = 0.39343 au = 3.3356 × 10^{-30} C m; $\mu(A^+B^-) > 0$)

molecule	μ/D			$\Delta\mu$/D	method[a]	ref
	NR	R	exptl			
LiH	2.3153[g]		2.3143 (2)[g]	−0.00026[e]	2D-DS	79a
				−0.00010[f]	2D-DS	
				−0.00036[d]	2D-DS	
HCl	1.4840	1.4987	1.1086 (3)[h]	+0.0147[e]	DF-LCAO	99e
HBr	1.016	0.915	0.8280 (6)[h]	−0.101[e]	PP-HF	241c
		0.758			PP-CI	241c
GeH		0.101	1.24[b]	<0.02	P-CI	268
		0.111		0.097	CEPA-1	270b
AgH		4.34[c]			PP-HF	215d
	5.11	4.64			PP-HF	183
HI	0.711	0.521	0.4477 (5)[h]	−0.19[e]	PP-HF	241c
		0.465			PP-CI	241c
AuH	4.67[c]				HF-LCAO	307
	5.24[d]				HF-LCAO	307
		2.87[c]			PP-HF	215d
	5.18	2.89			PP-HF	183
	5.800	3.346		−2.454[e]	PP-HF	241c
		2.005			PP-CI	241c
HgH	1.610	0.720		−0.89	PP-HF	241c
		0.557			PP-CI	241c
TlH	0.330	1.337		+1.007	PP-HF	241c
		1.372			PP-CI	241c
PbH	0.322	0.977		+0.655	PP-HF	241c
		1.212			PP-CI	241c
PbH_2	0.389	1.282		+0.893	PP-HF	241c
		1.642			PP-CI	241c

[a] See footnotes to Table IV. [b] Questionable.[268] [c] At R = 3.00 au. [d] At R_e(calcd). [e] Electronic reorganization. [f] Relativistic change of R. [g] The v = 0, J = 1 state of $^7Li^1H$. Theoretical value from: Roos, B. O.; Sadlej, A. J. *Chem. Phys.* **1985**, *94*, 43. Experimental value from: Rothstein, E. *J. Chem. Phys.* **1969**, *50*, 1899. [h] From: Lovas, F. J.; Tiemann, E. *J. Phys. Chem. Ref. Data* **1974**, *3*, 609.

other. A related phenomenon was the predicted, relativistic increase of the relative anisotropy

$$R = (J_{11} - (J_{22} + J_{33})/2)/J \qquad (54)$$

of the coupling tensor **J**, as observed in a comparison of $M(CH_3)_2$ (M = Cd, Hg)[365] or of solid MTe (M = Cd, Hg).[293g] The underlying mechanism seems to be the $\mathbf{J}_{sp}$ and, ultimately, a phase factor for $p_{1/2}$ AOs.[293d]

The relativistic increase of the s AO (corresponding to "Fermi contact") hyperfine integral reaches a factor of 3 around Hg to Pb, as first found by Breit in 1930[366] (for tables of HF and DF values, see ref 293d or Tables 5.8 of ref 2). This increases the spin–spin coupling between two heavy nuclei by an order of magnitude; the first observed ^1J(HgHg) in the largely 6s-bonded Hg_3^{2+} has a value of 139 600 Hz.[367]

The theory of ^1J(MM) and ^1J(MC) in tin and lead organometallics was discussed in ref 293f and that of ^1J(MM) in anionic clusters in ref 294f. The observed peculiarities of J(PbC) and J(PbPb) were attributed to a frontier-orbital effect, involving the highest occupied σ MO, which had some Pb 6s character and dominated the coupling trends.

It also was realized during these calculations[293d] that the symmetry rules, relating **J** to the molecular symmetry, required certain modifications.[294g]

Chemical Shifts. The relativistic analogue to Ramsey's theory of chemical shifts[368] has also been discussed.[369] In this case the most conspicuous and best known relativistic effect is the "heavy-atom shift", induced for instance by the heavy halogens, X (Br or I), on ^{1}H in HX or on ^{13}C in RX. The original suggestion was to use third-order perturbation theory,[370,371] with one matrix element of the Zeeman, hyperfine, and spin–orbit Hamiltonians. If relativistic MOs are used, second-order PT (with Zeeman and hyperfine operators) will do.[369] A transparent interpretation of the relativistic terms can then be obtained:[294d] spin–orbit effects induce otherwise forbidden contact hyperfine elements for (Zeeman allowed) $\pi \rightarrow \sigma$ (or $\sigma \rightarrow \pi$) excitations and also nonrelativistically forbidden Zeeman matrix elements for the (contact hyperfine allowed) $\sigma \rightarrow \sigma$ excitations.

A recent observation is the corresponding "heavy-atom shift of the heavy atom" itself[294e] ("HAHA") for ^{207}Pb atoms with lone pairs.

The nuclear magnetic shielding in free atoms was treated by Kolb et al.[372] Hegstrom[373] considered simple systems (H, H_2^+) at a deeper level. For H_2, see also ref 374.

Hyperfine Splittings. For relativistic calculations of the (magnetic dipole) hyperfine splittings in molecules, see Case et al.[126a,d]

Parity-Violation Effects. The parity nonconservation Hamiltonian[375] gives also an NMR chemical shift contribution which, if large enough, could produce a splitting between the nuclei (e.g., ^{195}Pt) in left- and right-handed chiral molecules.[295d] The PT violation effects in diatomic PbF were estimated in ref 214b.

Nuclear Quadrupole Coupling. Apart from various multiplicative relativistic correction factors,[376] little is known about specifically relativistic effects in this case.[377] An interesting particular case is that of the actinoid nucleus in actinyl ions, $^{234}UO_2^{2+}$ or $^{237}NpO_2^{2+}$, where it has been suggested that the $6p_{3/2}(1/2)$ semicore AO plays a dominant role,[293i] exceeding that of the 5f or 6d AOs. The unhybridized $6p_{1/2}$ AO has a spherical charge distribution and does not contribute.

Another particular problem is that of ^{197}Au(I) in the linear complexes[378] AuX_2– (X = F, Cl, CN), concerning the relative importance of Au 5d and 6p AOs. Sham et al.[378a] favor 6p and Guenzburger and Ellis,[378b] 5d. For

TABLE XIV. The "Soft Triangle" As Proposed by Ahrland[381a,e] (the Unitalicized Elements Are "Borderline" Elements and the Italicized Ones are "Soft"

	group								
	7	8	9	10	11	12	13	14	15
row 4		Fe(II)	Co	Ni	*Cu(I)*	Zn			As
row 5		*Ru*	*Rh*	*Pd*	*Ag*	*Cd*		Sn	Sb
row 6	Re	*Os*	*Ir*	*Pt*	*Au*	*Hg*	Tl(I) *Tl(III)*	Pb	*Bi*

a discussion on the 6p character in the isoelectronic Hg compounds, see ref 142b.

Mössbauer Isomer Shifts. This is probably the spectroscopic observable with the largest relativistic effects; see the earlier reviews.[379]

g tensors are intimately connected to spin–orbit effects but will not be discussed here.

V. Further Possible Examples and Open Problems

In this section we quote a number of further possible examples, often on the basis of circumstantial evidence only.

$4s^2$ and $5s^2$ Inert Pairs. In addition to the $6s^2$ inert pair discussed above, analogous compounds (such as GeO and SnO[51e]) are known for rows 4 and 5.[350c,380] While the relativistic 5s stabilization is not entirely negligible, the 4s stabilization due to the "d-block contraction" probably overweighs relativity on row 4.

Hardness and Softness. Ahrland[381a,e] points out the existence of a "soft triangle"; see Table XIV. The larger softness on row 6 might again be related to the relativistic destabilization of the 5d shell. It is interesting that $Tl^{3+}(5d^{10})$ should be "soft" but $Tl^{+}(6s^2)$ "borderline".

Notoya and Matsuda[381b] classified all monoatomic cations into three classes on the basis of their solvation free energies, ΔG, depending on their outer electron shell: (a) rare gas, (b) d^n, $n > 3$, and (c) $4f^{14}5d^{10}$. The strongly relativistic group c thus has a special position.

Glaser[381c] points out the curious fact that Tl(III) is the strongest acid ($pK_a = 1.2$) in group 13, despite having the largest ionic radius.

EA(*Z*) versus IP(*Z* + 1). Myers[383] found positive slopes for such plots for groups 1, 11, 13, 14, 16, and 17 but a negative slope for group 15.

The "18-electron rule" in organometallic chemistry is well-known. Would it have some relativistic "fine structure"?

Mercury being a liquid at room temperature, a fact attributed to the relativistic contraction of the filled $6s^2$ shell,[10,12] one may ask, why is gallium a liquid (T_m = 29.8 °C despite a high T_b = 2205 °C)? Perhaps the best answer is that already its crystal structure is very complicated. (The alkali metals have both low T_m *and* low T_b; for Cs they are 28.4 and 671 °C, respectively.[354])

Ashcroft[413] attributes the complicated crystal structure of gallium to core–core van der Waals interactions which are large compared to the *screened* Coulomb interactions in the metal.

The valency changes from Ag(I) to Au(III) could be studied by comparing the relative stabilities of MX_2^- and MX_4^- (M = Ag, Au; X = F, Cl, ...).

Similarly, the change from Sn(IV) to Pb(II) could be demonstrated by calculations on MX_6^{n-} (n = 2, 4; M = Sn, Pb). These explicit studies still do not exist.

The existing oxidation states were recently reviewed by Jørgensen.[384]

Mo and W compounds often have different structures, while the data in Table IX are taken from isostructural systems. This makes comparisons of the relativistic stabilities of their oxidation states more complicated, as emphasized in ref 18 and 19. One example is the different structures of stable MoO_3 and WO_3.[385a] Goodenough[385b] emphasizes the critical dependence of the solid-state chemistry of Mo on the radial extension of the 4d wave function. He suggests that due to the smaller Mo(4d)–O(2p) overlap, the Mo ions in the oxides are more strongly displaced, forming $(Mo{=}O)^{4+}$ oxomolybdenum cations, thus stabilizing the layered structure. W(5d) has larger overlap and therefore a smaller distortion, still breaking the cubic structure, but not going to a ReO_3 one.

The 5d functions are more diffuse than the 4d, already for the free atoms, both due to shell structure and relativity. In the octahedral model systems MH_6 it was found that for W the main maximum of the 5d wave function was moved from about 2 au to the bonding region around 3 au by relativistic effects (ref 113d, Figure 5; reproduced in ref 12).

Classical versus Nonclassical Hydrogens for 5d and 4d Metals. Structural differences occur between Mo and W also in free molecules. Of the polyhydrides, $MH_4(PR_3)_3$, those of Fe and Ru are "nonclassical" (contain H_2), while Os yields a "classical" hydride (with M–H bonds only).[385c] This would look like a straightforward consequence of the relativistic strengthening of the Os–H bond. Quite analogously, protonation of $(cp)(OC)_2M(\mu\text{-}PPh_2)Pt(CO)(PPh_3)$, M = Mo, gives a Mo–H–Pt bridgng hydrogen while for M = W, a terminal W–H bond results.[385d]

Under other circumstances, also the 5d metals, for example W[200d,l] or Ir,[385g] form nonclassical hydrogen complexes.

Equatorial versus Axial Bonds for Pentacoordinate Ru and Os. In addition to the data on MF_5 and MCl_5 in Table IX, the following problems exist: In the local tbp coordination about the metal in $[M_2(CO)_8]^{2-}$, the Ru–Ru bond in the sodium salt is asymmetric and, on one side, "equatorial", while the Os–Os bond in the potassium salt is "axial" on both sides.[385e] In $M(CO)_4(SbMe_3)$, the Sb–M bond is "axial" for Ru but "equatorial" for Os (Ru–Sb = 261.87 (9), Os–Sb = 261.2 (2) pm).[385f]

Ag versus Au: Gold Chains. Ahrland et al.[386] find that the tetrahydrothiophene complex $Au((CH_2)_4S)I$ forms chains, but the corresponding Ag compound tetramers of the cubane type. The M–S and M–I distances were 22 and 33 pm shorter, respectively, for Au than for Ag. This resembles the situation in the diatomic hydrides, with Au–H = 152 and Ag–H = 162 pm.

Ahrland et al.[386] also point out that AgCl and AgBr have the NaCl structure, while AuCl and AuBr form zigzag chains.[387] The problem awaits a theoretical analysis.[421,422]

In the three-coordinated complexes MCl(PP) (M = Ag, Au; PP = 2,11-bis((diphenylphosphino)methyl)-benzo[c]phenanthrene), the Au–P of 231 pm also is shorter than Ag–P (by 10 and 15 pm for P_1 and P_2, respectively). Now also the PMP angles are very dif-

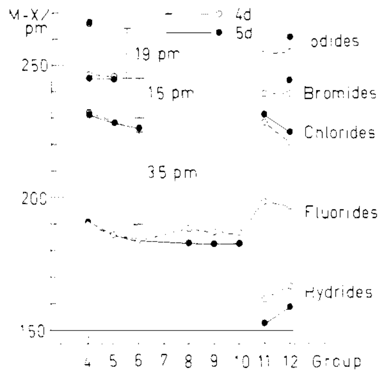


Figure 16. Experimental bond lengths for 4d and 5d transition-metal halides and hydrides. The differences of the r_{cov}(Pauling) are given as vertical bars.

ferent, 175.7 (1) and 140.7 (1)° for Au and Ag, respectively, making this one of the few candidates for a large relativistic effect on a bond angle.[388]

The Au–P in $Au(C_2Ph)(PPh_3)$ is 228 pm,[389a] indicating an absence of axial strain in AuCl(PP).

MRu_4 Clusters (M = Ag, Au). Salter and Stone[389b] find that in the metal clusters $H_3MRu_4(CO)_{12}(PPh_3)$ (M = Ag, Au) the gold cluster, 1, has an Au atom edge-bridging (μ_2) the Ru_4 tetrahedron, while the μ_3 Ag atom in the silver cluster, 2, caps a Ru_3 face. The three hydrogen atoms similarly are μ_2 and μ_3 in 1 and 2, respectively.

The gold–oxygen complexes $Au(O_2)$ are found from ESR evidence to have a symmetric, side-on structure while both $Cu(O_2)$ and $Ag(O_2)$ have bent, end-on structures.[390]

Mercurium captans ("seizing mercury") is the generic term for mercaptans.[391] The question is, why should the Hg–S bond be so strong? (The formation constant for CH_3HgSR is 10^{14}–10^{18}.) No theoretical analysis seems to exist.

Two-Coordination of Mercury. As said earlier,[12] the dominant two-coordination of Hg has been attributed to either a large s–p separation,[51b] favoring sp hybridization over sp^n, $n > 1$, or to the smaller s–d separation (compared to Cd).[351,392] Both changes involve relativistic effects, the 6s stabilization and the 5d destabilization.[68]

Tossell and Vaughan[393] attribute the two-coordination of Hg to the 5d level, approaching the ligand *np* and leading to too much Hg(5d)–L(*np*) antibonding for the tetrahedral coordination.

The same problem of coordination numbers occurs for the isoelectronic neighboring systems, such as $TlBr^{2+}$, $TlBr_2^+$, $TlBr_3$, $TlBr_4^-(T_d)$, $TlBr_5(OH_2)^{2-}$, and $TlBr_6^{3-}$. The Tl–Br of 248, 251, 256, 273 ((4 × 278) + (1 × 252))/5), and 276 pm for CN = 2–6, respectively,[381c] are closely similar to the Hg–Br of 248 (in the solid), 252, and 259 pm for CN = 2–4 (see Wells[350c]) in the isoelectronic $HgBr_2$, $HgBr_3^-$, and $HgBr_4^{2-}$, respectively.

When passing from Hg to Tl, the 5d should become less important and the 6p more important.

The octahedral Hg(II) complexes also have a tendency to distort, forming two short and four long bonds[381d] while Zn(II) and Cd(II) do not. It is not yet clear whether Tl(III) distorts.[381c]

Although detailed analyses of the bonding in linear mercury compounds have been presented by De Kock et al.,[142b] no comparative theoretical studies of the formation enthalpies for CN = 2 and CN = 4 exist.

Bond Lengths of 4d and 5d Transition Metals. We return to the data in Table IX and show the experimental M–X (X = halogen) and M–H bond lengths in Figure 16. It is interesting that the M–F and M–H bond lengths for groups 8–12 are shorter for the 5d metal than for the 4d metal, like the M–PR_3 ones in Table VIII. (In parallel with this trend, the stretching force constants, *k*, show an increase.[394]) The other M–X (X = Cl, Br, I) show the opposite trend, like the M–C in Table VIII and the M═N and M–M ones in Table IX.[418,420]

Zr and Hf are strikingly similar. Our current explanation[69] is that the relativistic and shell-structure trends almost exactly cancel.

Astatine chemistry should be strongly influenced by 6p spin–orbit splitting (3.47 eV[37]). In a covalent compound, for example HAt, Pitzer's spin–orbit weakening near R_e (see section IV.B) should diminish D_e. The experimental D_e is unknown,[395a] and the only theoretical values are REX estimates.[293c]

Radon. Stein[395b] presents evidence that radon is a metalloid element and that it would form RnF^+ and

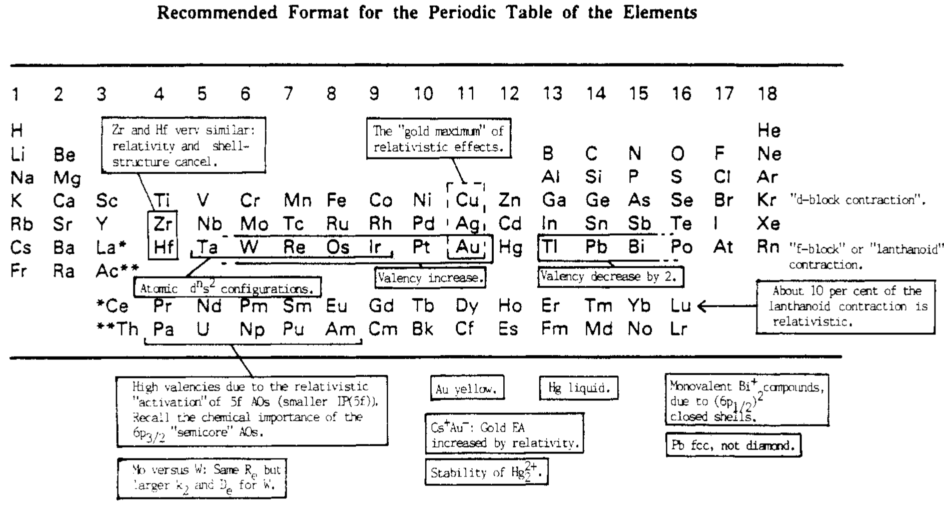


Figure 17. Relativity and the Periodic Table: a summary.

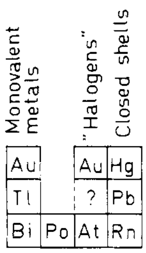


Figure 18. A version of the Periodic System for the elements $_{79}$Au to $_{86}$Rn, emphasizing the $6s^2$ and $(6p_{1/2})^2$ closed shells.

Rn^{2+} in its reactions with halogen fluorides; the relativistic $6p_{3/2}$ orbital energy is only 90% of the nonrelativistic one.[37] This should facilitate the oxidation states Rn(II) and Rn(IV).

VI. Summary: Relativistic Effects in the Periodic Table

Many of the points discussed in this review are summarized in Figure 17.

This figure summarizes the points made above on the change from $5s^n$ to $6s^{n+1}$ electron configurations for free atoms (Table II), the valency increase from Ag(I) to Au(III) etc.,[10] the valency decrease from Sn(IV) to Pb(II) (section III.E), the "gold maximum" of relativistic effects (Figure 3), the role of relativity in the lanthanoid contraction (section III.A, Table VII), the comparison of Zr and Hf (section V), the comparison of R_e, k_2, and D_e for single bonds to Mo and W (section III.A, section IV.A, Table IV, and section V), the color of gold (Figure 15, section IV.E), the existence of ionic CsAu (sections II.B and III.D), the stability of Hg_2^{2+},[10,148g,233c] the crystal structure of lead (section III.D), the existence of monovalent Bi compounds (section II.B), and, eventually, the low boiling point of Hg.[10] The d-block and f-block contractions were discussed in section II.B. These two periodic trends are shell-structure ones, and are not due to relativity.

The actinoids (An) (from Th to Am) are a fascinating chapter. They show, in their higher valence states, relativistically "activated" 5f and 6d shells (see Figure 7 of ref 10) and also considerable hybridization of the $6p_{3/2}$ semi-core shell (for a review of existing molecular calculations on Ln and An compounds, see ref 396 and 414 and for band structure calculations see ref 339b.)

Finally, we take the liberty of presenting in Figure 18 a rather original version of the Periodic System for the elements $_{79}$Au to $_{86}$Rn. The aspect emphasized is the effects due to the closed $6s^2$ and $(6p_{1/2})^2$ shells. The experimental facts fitting this table are the existence of aurides (like Cs^+Au^-) and of monovalent bismuth compounds, and the small, spin–orbit-decreased D_e of lead compounds, for example PbH and Pb_2[176b,c,e,397] or BiH^+.[175h,417]

For the superheavy elements 111–118 this classification may be even more fitting.

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