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Relativistic effects on molecular structure: methyl derivatives of the fourth main-group elements

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The compounds ZR_4 with $R = H, CH_3$, and $Z = C$, Si, Ge, Sn or Pb have been studied in high-quality Hartree-Fock calculations. Relativistic effects have been accounted for, using the Breit-Pauli Hamiltonian and first-order perturbation theory. Relativity causes a shortening of the Z-R distance of up to 10 pm in PbH_4, whereas the effect on the breathing force constant is more complex.

Key words: Structure optimization — *Ab initio* calculations — Perturbation theory — Relativistic effects

1. Introduction

The attention of computational quantum chemistry has long been concentrating on the upper half of the Periodic table. With increasingly more powerful computational resources, including efficient program codes, it is now becoming possible to study systems with a large number of electrons, as well as atomic orbitals with high angular momenta. This opens the possibility of studying heavy elements, for which relativistic effects are known to be important.

In the pioneering work by Desclaux and Pyykkö [1, 2], relativistic effects on the bond distance and breathing force constant were studied for the hydrides of the fourth main-group elements, down to and including the superheavy element (114). While their calculations proved beyond doubt that relativistic effects are important for the heavier members of the series, the one-center expansion method

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used in their calculations is not sufficiently accurate to produce quantitatively reliable results.

In the present study, we have addressed the same problem with large multi-center basis sets for the compounds CH_4 to PbH_4. We have also extended the calculations to include the analogous methyl compounds $C(CH_3)_4$ to $Pb(CH_3)_4$. Relativistic effects were accounted for by means of first order perturbation theory [3, 4] using the Breit-Pauli Hamiltonian. At this level of approximation the spin-orbit interaction is neglected. The relativistic correction to the energy contains only two terms; the mass-velocity correction and the Darwin interaction term.

2. Details of the calculations

All the molecules were studied within the Hartree-Fock level of approximation, using the Direct SCF code DISCO [5]. The Hartree-Fock method ought to perform well for the molecules considered here, in particular as our main interest concerns shifts in the calculated parameters. The different basis sets used are summarized in Table 1. A basis for Pb was optimized for the $p^2(^3P)$ state, since none was available in the literature. The optimized exponents and contraction coefficients for Pb are shown in Table 2.

For the methyl compounds down to and including $SnMe_4$, the calculations were carried out with the large, polarized basis sets C3 and H5 on the methyl groups.

Table 1. Basis sets used in the calculations

Mnemonics	Reference	Primitive basis	Augmented by	Total No. GTO	Contraction	Total No. CGTO
H1	6	3s		3	3s	2
H2	7	7s		7	3s	3
H3	7	7s		7	4s	4
H4	7	7s	1p[a]	10	3s1p	6
H5	7	7s	1p[a]	10	4s1p	7
C1	8	7s3p		16	4s2p	10
C2	9	10s6p		28	6s4p	18
C3	9	10s6p	1d[b]	34	6s4p1d	24
Si1	10, 11	12s9p	1d[c]	45	8s6p1d	32
Ge1	12	14s11p6d		83	10s8p4d	58
Sn1	13	15s11p6d	2d[d]	96	12s9p7d	81
Sn2	13	15s11p6d	2d[d]2f[e]	116	12s9p7d2f	101
Sn3	13	15s11p6d	2d[d]2f[e]	116	15s11p8d2f	116
Sn4	13	15s11p6d		84	12s9p5d	69
Pb1	—	23s18p10d5f		187	17s15p10d5f	172

[a] $\zeta_p = 0.8$
[b] $\zeta_d = 0.63$ (Ref. [14])
[c] $\zeta_d = 0.30$
[d] $\zeta_d = 0.27$; $\zeta_d = 0.09$
[e] $\zeta_f = 1.20$; $\zeta_f' = 0.50$

Table 2. CGTO numbers, exponents, and contraction coefficients for Pb (23, 18, 10, 5/17, 15, 10, 5) basis. This basis set gives a total energy for $(p^2)^3P$ of −19523.77975 a.u. (uncontracted) and a virial ratio of −1.9999999070

	s			*p*	
1	63 612 712.2641970	0.0000049	1	160 931.7283350	0.0000609
1	12 076 671.3328490	0.0000275	1	36 370.3848040	0.0005840
1	3 052 746.8374960	0.0001392	1	11 470.7941130	0.0035529
1	874 066.8922440	0.0005956	1	4 258.1847480	0.0165114
1	286 681.1852060	0.0021321	2	1 762.3491140	1.0000000
1	105 184.1750840	0.0067151	3	792.8505230	1.0000000
1	41 735.8531330	0.0195108	4	378.4391990	1.0000000
2	17 331.5413390	1.0000000	5	188.0376840	1.0000000
3	7 468.5109620	1.0000000	6	95.6599740	1.0000000
4	3 350.3766480	1.0000000	7	49.0122890	1.0000000
5	1 555.3158280	1.0000000	8	25.5998970	1.0000000
6	737.0321400	1.0000000	9	12.7178080	1.0000000
7	338.9535280	1.0000000	10	6.4341370	1.0000000
8	172.4121030	1.0000000	11	3.0776940	1.0000000
9	87.2758610	1.0000000	12	1.4907950	1.0000000
10	39.1958080	1.0000000	13	0.6640590	1.0000000
11	20.7754380	1.0000000	14	0.1765020	1.0000000
12	9.0637470	1.0000000	15	0.0596280	1.0000000
13	4.7529010	1.0000000			
14	1.6514890	1.0000000			
15	0.7934060	1.0000000		*d*	
16	0.1694010	1.0000000			
17	0.0667700	1.0000000	1	1 767.2039100	1.0000000
			2	532.7929270	1.0000000
			3	204.4681470	1.0000000
	f		4	87.7670060	1.0000000
			5	39.8290280	1.0000000
1	156.4827160	1.0000000	6	17.7878360	1.0000000
2	52.3134710	1.0000000	7	7.9717980	1.0000000
3	20.5024680	1.0000000	8	3.4311070	1.0000000
4	8.2003440	1.0000000	9	1.3498150	1.0000000
5	3.0528190	1.0000000	10	0.4685330	1.0000000

Table 3. Basis set dependence of the bond distance and force constant in CH_4. The relativistic corrections are included in the energies and distances listed

Basis[a]	−*E* (Hartree)	*R* (pm)	−Δ*R* (fm)[b]	*k* (a.u.)
C2H5	40.222	107.94	11.5	0.3843
C3H2	40.218	108.73	9.9	0.3787
C3H3	40.221	108.39	10.3	0.3766
C3H4	40.226	108.37	10.8	0.3759
C3H5	40.228	108.26	10.8	0.3773

[a] For notation, see Table 1

[b] Relativistic correction to the geometry

Table 4. Basis set dependence for $GeMe_4$ and $SnMe_4$

Basis	$-E_{rel}$	$-\Delta E_{rel}$	$R_{M\text{-}C}$ (pm)	R_{rel} (pm)	k_{rel} (a.u.)
Ge1C3H5	2255.22	21.3688	197.0	0.51	0.198
Ge1C1H1	2254.97	21.3684	197.3	0.52	0.197
Sn1C3H5	6180.73	142.239	217.4	1.58	0.154
Sn1C1H1	6180.47	142.235	215.0	1.54	0.153

As indicated by a basis set study on methane, shown in Table 3, the results obtained with that basis are reasonably well converged to the Hartree–Fock limit. $GeMe_4$ and $SnMe_4$ were also studied with the smaller, double-ζ type basis set C1H1. The results, summarized in Table 4, suggest that only minor differences would occur if the smaller basis set was used for GeH_4. In SnH_4, the situation is a little different. The change of basis has a rather significant influence on the geometry. There is no a priori reason why the metal-carbon bond in $SnMe_4$ should require a more extensive carbon basis set than in $GeMe_4$. We may therefore conclude that the shift in SnC bond length upon changing the carbon basis is an effect of the basis on Sn, which is of somewhat poorer quality than for the other members of the series. Accordingly, the calculations on $PbMe_4$ were carried out with the double-zeta basis on methyl. To check if f polarization functions would be necessary for the heavier elements, SnH_4 was studied with the two basis sets Sn1 and Sn2. The results, shown in Table 5, indicate only a minute effect of f orbitals, and no such functions were therefore included (except for Pb). Using a completely uncontracted basis (Sn3) also gave very small changes in the computed bond distance. The relativistic contribution to the energy changed by 0.7 Hartree, however. This seems to be a result of the increased flexibility near the nucleus, and probably has very little effect on most molecular properties. The previously mentioned deficiencies of the Sn1 basis, encountered in the $SnMe_4$ calculations, therefore seem to be related to the valence region rather than to the inner, contracted part.

In all our calculations, only geometries of T_d symmetry were considered. For the methyl compounds, only the Z-C distances were varied, keeping the methyl groups at standard geometry (R_{CH}–1.094 Å, ZCH angles perfectly tetrahedral, hydrogens in a staggered orientation with respect to the other three methyl groups). For most molecules in the study, only three different bond lengths were considered, in grids with step lengths of 0.02-0.03 Å, always enclosing the minimum.

3. Results

Calculated Z-H distances for the hydrides are shown in Table 6, along with experimental geometries and results of the previous OCE calculations [1]. Our results are seen to compare rather favorably with the experimental ones. No experimental data are available for PbH_4, but a value of 175.4 pm has been indirectly deduced [1] by comparing the experimental distances in PbH, SnH

Table 5. Properties of SnH_4, calculated with different basis sets

Basis	$-E$ (Hartree)	$-\Delta E_{rel}$	R (pm)	$-\Delta R$ (pm)	k (a.u.)
Sn1H5	6024.559	142.182	170.5	2.12	0.1532
Sn2H5	6024.565	142.183	170.5	2.16	0.1534
Sn3H5	6024.604	141.488	170.3	2.10	0.1533

and SnH_4. However, that deduced distance does not compare particularly well with our calculated value. In light of the good agreement for the other members of the series, we expect our calculated distance of 170.3 pm to be the more reliable one, and to constitute the best prediction of the geometry for PbH_4.

Rather remarkably, our non-relativistic energies are all 0.3–0.8 Hartree better than those of [1]. The energy computed for the central atom with the one-center expansion is certainly better than ours, so apparently there are serious deficiencies in the OCE description of hydrogen atoms and of the bonding. This might explain why the distances computed by that approach differ so much from ours (and from experiment).

Similar results for the tetra-methyl compounds ZMe_4 are shown in Table 7. In all cases, the calculated results are in very good agreement with the experimental data.

Table 6. Calculated geometries of the ZH_4 hydrides, compared with experimental values

Basis on Z	C3	Si1	Ge1	Sn2	Pb1
no. of GTO	78	85	123	156	227
no. of CGTO	52	60	86	129	200
$-E_{nr}$ (H)[a]	4.02128+1	2.91249+2	2.07763+3	6.02456+3	1.95259+4
OCE[a,b]	3.95320+1	2.90313+2	2.07680+3	6.02427+3	1.95253+4
$-\Delta E_{rel}$ (H)[a]	1.47−2	5.67−1	2.13+1	1.42+2	1.14+3
OCE[a,b]	1.30−2	6.00−1	2.11+1	1.48+2	1.37+3
r (pm)	108.3	148.2	152.1	170.5	170.3
OCE[b]	109.9	157.2	158.6	176.2	179.7
exp	108.6[c]	148.1[d]	152.7[e]	170.1[e]	(175.4)[f]
theor.	108.3[h]	147.4[g], 146.8[h]		171.5[i]	174.3[i]
$-\Delta r$ (pm)[a]	1.0−2	6.6−2	7.0−1	2.1+0	1.0+1
OCE[a,b]	0	1.0−1	1.0−0	4.0+0	1.1+1
ECP[i]				1.7+0	8.4+0

[a] Entry shows mantissa and exponent in a decimal representation
[b] Dirac-Fock calculation using one-center expansion, Ref. [1]
[c] Ref [15]
[d] Refs. [16, 17]
[e] Ref. [18]
[f] Value deduced [1] from experimental geometries of PbH, SnH and SnH_4
[g] Ref. [19]
[h] Ref. [20]
[i] Relativistic effective core potentials. Unpublished results (M. Pelissier; Thesis 1984)

Table 7. Calculated geometries of the ZMe_4 compounds, compared with experimental values

Basis on Z	C3	Si1	Ge1	Sn1	Pb1
Basis on Me	C3H5	C3H5	C3H5	C3H5	C1H1
no. of GTO	290	301	339	352	275
no. of CGTO	204	212	238	261	224
$-E_{\text{rel}}$ (H)	1.9647+2	4.4815+2	2.2552+3	6.3230+3	2.0824+4
$-\Delta E$	7.34−2	6.59−1	2.14+1	1.42+2	1.14+3
r_{rel} (pm)	154.0	190.2	197.0	215.0	224.7
r_{exp}	153.9[a]	187.5[b]	198[c]	214.3[d]	223.8[e]
Ref. [26][f]	151.9	184.8	190.3		
$-\Delta r_{\text{rel}}$ (pm)	4.0−3	6.6−2	5.1−1	1.8+0	4.5+0

[a] Ref. [21]
[b] Ref. [22]
[c] Ref. [23]
[d] Ref. [24]
[e] Ref. [25]
[f] Theoretical values (FSGO calculation with pseudopotentials)

In addition to equilibrium geometries the breathing vibrational force constants may be estimated from calculations using the full molecular symmetry. However, it must be borne in mind that force constants are much more sensitive to the three-point parabolic fit than equilibrium geometries. In order to obtain correct force constants in such a procedure, the grid used must be properly centered around the minimum [27]. The fact that no such centering was done in the present work hardly affects the quoted geometries within the given accuracy. One can easily show that the error in predicted geometry would be

$$\Delta r = \alpha(\delta^2 - S^2/3)/(2k + 2\alpha\delta) \tag{1}$$

where δ is the offset of the true minimum from the center of the grid, S is the step length and the potential energy V is given by

$$V = \frac{k}{2} q^2 + \frac{\alpha}{6} q^3. \tag{2}$$

With the value of S used here, $|\delta| < S/2$ and with reasonable values of k and α, Δr would normally be less than 5×10^{-4} Å. The error on the force constant, on the other hand is given by

$$\Delta k = \alpha\delta \tag{3}$$

and could amount to 10% of k. To improve the situation, the anharmonicity constant α may be taken from model calculations or from experiments, and used to evaluate improved force constants.

The anharmonicity is also essential for evaluating the relativistic effect on the force constants. The relativistic energy may be written as

$$V_{\text{rel}} = V_{\text{nr}} + \Delta V \tag{4}$$

where the non-relativistic term V_{nr} is given by Eq. 2 and the relativistic correction may be expressed as

$$\Delta V = C_0 + C_1 q + \tfrac{1}{2} C_2 q^2. \tag{5}$$

Clearly, the correction to the force constant has two contributions, one due to the curvature of the relativistic energy term, C_2, and one from a term similar to (3), caused by the relativistic shift of geometry. The form of the total correction is

$$\Delta k_{rel} = C_2 + \alpha \Delta r_{rel} \approx C_2 - \alpha C_1 / k. \tag{6}$$

The two terms are normally of similar magnitude but opposite sign, and both must be evaluated to determine the relativistic effect on the force constants. In order to get an idea of the qualitative behavior of ΔV, the relativistic corrections to the energies of SnH_4 and PbH_4 have been evaluated over a wide range of distances. The results, shown in Fig. 1 clearly demonstrate the sharp drop of ΔV at small distances. For SnH_4, the function goes smoothly towards the asymptotic limit of infinite separation. The important qualitative features in the region of interest are (a) the positive slope (C_1 in (5) and (6)), and (b) the negative curvature (C_2). The behavior of PbH_4 is remarkably different. The relativistic energy correction is almost linear in the region of the energy minimum, but is sharply convex both at shorter and at longer distances. Eq. (5) therefore does not accurately model the situation in PbH_4.

Tables 8 and 9 show the calculated coefficients used in the force constant correction (6) for ZH_4 and ZMe_4. The reduction of force constants that one would assume to take place - due to the negative sign of C_2 - is largely cancelled by the combined effect of anharmonicity and bond shortening. As discussed above, PbH_4 is extreme in this context. Therefore, the force constant for PbH_4 was also evaluated from a parabolic fit to the relativistic energy near the minimum. The calculated force constants for ZH_4 and ZMe_4 are summarized in Tables 10 and 11, together with previous experimental and theoretical results. The agreement

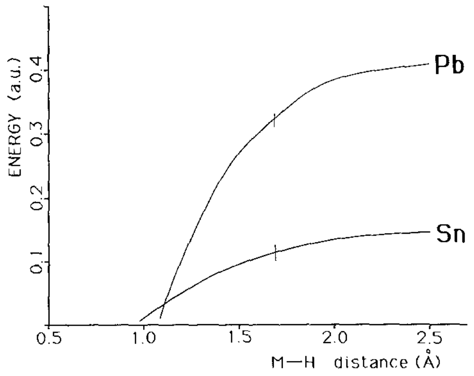

Fig. 1. Plots showing relativistic corrections to the energies of PbH_4 and SnH_4 as functions of the bond distance. The equilibrium geometries are indicated in the graphs. (The zero point on the energy scale has been shifted.)

Table 8. Coefficients used in evaluating the relativistic effects on force constants in ZH_4. The constants refer to Eqs. (2), (5) and (6)

	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
k (H Å^{-2})	5.512	3.103	2.791	2.470	2.093
α (H Å^{-3})	−29.55[a]	−13.19[a]	−11[b]	−9.06[c]	−8.22[c]
C_1 (H Å^{-1})	6−4	1.9−3	2−2	4.9−2	2.4−1
C_2 (H Å^{-2})	−3.2−3	−8.1−3	−3.6−2	−1.52−1	−2.0−1
Δk (H Å^{-2})	0	+5−4	+4−2	+4−2	+7.4−1

[a] Theoretical value, Ref. [28]
[b] Interpolated value
[c] Theoretical value, this work

Table 9. Coefficients used in calculating the relativistic corrections to the force constants of ZMe_4, according to Eq. (6). The anharmonicity constants α were taken from Table 8, and scaled with the ratio of harmonic force constants $k(ZMe_4)/k(ZH_4)$

	CMe_4	$SiMe_4$	$GeMe_4$	$SnMe_4$	$PbMe_4$
k (H Å^{-2})	4.590	3.075	2.730	2.353	2.118
α (H Å^{-3})	−24.6	−11.8	−10	−7.8	−7.0
C_1 (H Å^{-1})	5−4	1.8−3	1.3−2	3.5−2	8.7−2
C_2(H Å^{-2})	−1−3	−1.2−3	−6.7−2	−1.6−1	−2.4−1
Δk (H Å^{-2})	+1−3	0	0	−2−2	+7.5−2

Table 10. Calculated breathing force constants for ZH_4, compared with previous experimental and theoretical results. Units are aJ Å^{-2}

	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
This work	6.00	3.38	3.09	2.74	3.09[a], 3.71[b]
OCE[c]	5.4	2.2	2.4	2.0	2.1
NR[d]	5.95[e], 5.64[f]	3.36[e,g], 3.02[f]			
Expt.	5.84[h]	2.84[i]	2.81[i]	2.27[j]	

[a] Calculated using Eq. (6)
[b] Evaluated at the relativistic equilibrium geometry
[c] Relativistic calculation using a one-center expansion, Ref. [1]
[d] Non-relativistic theoretical work
[e] Ref. [20]
[f] Ref. [28]
[g] Ref. [19]
[h] Refs. [29, 34]
[i] Ref. [31]
[j] Ref. [32]

Table 11. Calculated (relativistic) force constants in aJ Å^{-2} for ZMe_4, compared with experimental results and with previous calculations

	CMe_4	$SiMe_4$	$GeMe_4$	$SnMe_4$	$PbMe_4$
This work	5.00	3.35	2.98	2.54	2.14
Expt.	4.64[a]	3.22[b]	2.86[b]	2.32[b]	1.92[b]
Theor.[c]	5.24	3.44	3.08		

[a] Ref. [33]
[b] Ref. [34]
[c] Non-relativistic FSGO calculations using pseudo-potentials, Ref. [26]

with experiment is generally as good as one may expect from calculations at the Hartree-Fock level of approximation. The result obtained for PbH_4 when using Eq. 6 differs somewhat from that obtained directly from the relativistic energy. However, both values confirm the increase as compared with SnH_4, which is also observed in the previous OCE calculations [1].

4. Conclusions

Our rather simple approach to molecular relativistic effects - Hartree-Fock calculations and first order perturbation theory using the Breit-Pauli Hamiltonian - has been shown to yield results in very good agreement with experiment, even for systems as heavy as $PbMe_4$. All molecules studied in this work are closed-shell systems, and, therefore, the conclusion above does not apply to cases where spin-orbit coupling is crucial.

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References

1. Desclaux JP, Pyykkö P (1974) Chem Phys Lett 29:534
2. Pyykkö P, Desclaux JP (1977) Nature 266:336
3. Cowan RD, Griffin DC (1976) J Opt Soc Am 66:1010
4. Matcha RL (1976) J Chem Phys 65:1962
5. Almlöf J, Faegri K Jr, Korsell K (1982) J Comput Chem 3:385
6. Huzinaga S (1965) J Chem Phys 42:1293
7. van Duijneveldt FB (1971) IBM Res Report RJ945
8. Roos B, Siegbahn P (1970) Theoret Chim Acta 17:209
9. Dunning TH Jr (1971) J Chem Phys 55:716
10. McLean AD, Chandler GS (1980) J Chem Phys 72:5639
11. Veillard A (1968) Theoret Chim Acta 12:405
12. Huzinaga S (1977) J Chem Phys 66:4245
13. Dunning TH Jr: unpublished results
14. Roos B, Siegbahn P (1970) Theoret Chim Acta 17:199
15. Gray D L, Robiette AG (1979) Mol Phys 37:1901

16. Lovejoy RW, Olson WB (1972) J Chem Phys 22:643
17. Kattenberg HW, Oskam A (1974) J Mol Spectrosc 49:52
18. Tables of Interatomic Distances (The Chemical Society, London 1965)
19. Komornicki A (1984) J Am Chem Soc 106:3114
20. Wiberg KB, Wendoloski JJ (1984) J Phys Chem 88:586
21. Beagley B, Brown DP, Monaghan JJ (1969) J Mol Struct 4:233
22. Beagley B, Monaghan JJ, Hewitt TG (1971) J Mol Struct 8:401
23. Brockway LO, Jenkins HO (1936) J Am Chem Soc. 58:2036
24. Nagashima M, Fuiji H, Kimura M (1973) Bull Chem Soc Jpn 46:3708
25. Oyamada T, Lijima T, Kimura M (1971) Bull Chem Soc Jpn 44:2368
26. Toman JJ, Frost AA, Topiol S, Jacobson S, Ratner MA (1981) Theoret Chim Acta 58:297
27. Pulay P (1977) In: Schaefer III HF (ed) Modern theoretical chemistry. Plenum, New York, and references cited therein
28. Schlegel HB, Wolfe S, Bernardi F (1975) J Chem Phys 63:3632
29. Jones LH, McDowell R S (1959) J Mol Spectrosc 3:632
30. Kuchitsu K, Bartell LS (1962) J Chem Phys 36:2470
31. Duncan JL, Mills IM (1964) Spectrochim Acta 20:523
32. Levine IW, Schiffer H (1965) J Chem Phys 43:4023
33. Snyder RG, Schachtschneider JH (1965) Spectrochim Acta 21:169
34. Watari F (1978) Spectrochim Acta 34A:1239