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Relativistic all-electron molecular Hartree–Fock–Dirac–(Breit) calculations on CH_4, SiH_4, GeH_4, SnH_4, PbH_4

O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort
Laboratory of Chemical Physics and Materials Science Centre, University of Groningen,
Nijenborgh 16, 9747 AG Groningen, The Netherlands

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Summary. Results and details of molecular Fock–Dirac–(Breit) calculations on CH_4, SiH_4, GeH_4, SnH_4, and PbH_4 obtained with the MOLFDIR© program package are presented and compared with other calculations and experimental results. The relativistic ground state energies (including the Breit interaction) of the atoms C, Si, Ge, Sn, and Pb, necessary for reference purposes, have been calculated using a small relativistic CI. One of our findings is that for the heavier systems perturbation theory over-estimates the relativistic bond length contraction. The Breit interaction has only a small effect on the bond lengths.

Key words: Relativistic *ab initio* calculations – Hartree–Fock–Dirac method – Breit interaction – Tetrahedral hydrides

1 Introduction

The *ab initio* study of relativistic effects in molecular systems is a relatively new field of research. Only in the past decennium various calculations based on relativistic quantum mechanics have been performed [1–4 and references therein]. Most of these calculations concern atomic systems, a few concern diatomic molecules. Applications to polyatomic molecular systems have been sparse except for calculations based on local density or other more approximate methods.

Approaches to the study of relativistic effects include perturbation theory, relativistic pseudo-potential techniques, relativistic local density methods and Fock–Dirac calculations. We use the all-electron Hartree–Fock–Dirac model followed by a small relativistic configuration interaction (CI). This allows the results to serve as reference for more approximate methods. The method also enables the study of the effects of the Breit interaction.

In this article we present all-electron Hartree–Fock–Dirac SCF-results of calculations on the series CH_4, SiH_4, GeH_4, SnH_4, and PbH_4. Some calculations published earlier by some of us [4, 5], concerning CH_4, SiH_4, GeH_4, have been improved. For reference purposes, we also present results of small relativistic CI calculations on the group IV atoms C through Pb. Among the results are relativistic bond lengths, bond energies and the effect of the Breit interaction on these properties.

2 Theory

In this section the basic equations underlying our method are presented and the way we solve them is described. Some details of the MOLFDIR© (Molecular Fock–Dirac) program package are given (type of basis functions, kinetic and atomic balance, and general contraction); more details on the open shell and the COSCI (Complete Open Shell Configuration Interaction) method used, symmetry handling, and implementation details can be found elsewhere [5–7].

2.1 General

The time-independent Dirac equation for one-electron molecular systems [8, 9] can be written as (in atomic units):

$$(c\alpha \cdot \boldsymbol{p} + \beta mc^2 + V)\varphi = \varepsilon\varphi \tag{1}$$

The α and β are the four matrices defined by:

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2}$$

in which σ is the vector of Pauli spin-matrices, V is the potential energy $V(\boldsymbol{r}; \boldsymbol{R})$ due to the nuclei at $\boldsymbol{R}$, c is the speed of light in vacuum (the value 137.03602 a.u. is used in the calculations) and m is the rest-mass of the electron. $\varphi(\boldsymbol{r})$ is a four-component spinor which is conveniently written as a combination of two bi-spinors:

$$\varphi = \begin{pmatrix} \varphi^L \\ \varphi^S \end{pmatrix} \tag{3}$$

L and S refer to 'large' and 'small' component, respectively, because to first-order approximation:

$$\varphi^S \approx \frac{1}{2c}\sigma \cdot \boldsymbol{p}\varphi^L \tag{4}$$

for positive energy states.

One can show from quantum electrodynamics [10, 11] that an approximate relativistic many-electron equation (the Dirac–Coulomb–Breit equation) is given by:

$$\left(\sum_i (\alpha_i \cdot \boldsymbol{p}_i + \beta_i mc^2 + V_i) + \sum_{i<j}\left(\frac{1}{r_{ij}} + B_{ij}\right)\right)\psi = E\psi \tag{5}$$

The two-electron interaction in this equation consists of the usual Coulomb term and the Breit term. The latter term, which for chemical systems contributes numerically only marginally to the total energy compared to the Coulomb term [10], is given by:

$$B_{ij} = -\frac{1}{2}\left\{\frac{\alpha_i \cdot \alpha_j}{r_{ij}} + \frac{(\alpha_i \cdot \boldsymbol{r}_{ij})(\alpha_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^3}\right\} \tag{6}$$

The Breit term can be approximated by the Gaunt term [2, 10, 12], which is just twice the first term in Eq. (6). In this article we use the Gaunt term only.

2.2 The relativistic open shell SCF *equations*

The relativistic open shell SCF equations can formally be derived in the same way as their non-relativistic counterparts [13]. The one-electron Schrödinger operators are replaced by Dirac operators, the interaction terms appear on the diagonal of a four-component matrix and the scalar spin-orbitals become four component spinors. Fundamentally there is of course a major difference when variational methods are applied to find approximate solutions. In the search for stationary points in the parameter space of the energy functional in the case of the Dirac equation, there is no variational principle that guarantees that one will never find energies lower than the exact (positive) ground state energy.

The Breit interaction term can – technically – be included in the hamiltonian and thus be used in the variational process. Alternatively, its effect can be included afterwards by perturbation theory. It is still a matter of discussion whether it is legitimate to include the Breit term in the variational process [14, 15 and references therein].

2.3 Basis functions

The MOLFDIR program package uses two distinct sets of, usually atom-centered, scalar (contracted) cartesian gaussian functions: a 'large component' set $\{g_i^L\}$ and a 'small component' set $\{g_i^S\}$. The required two-electron repulsion integrals are calculated over the functions belonging to these sets.

From these two scalar sets two new sets of symmetry adapted molecular Dirac spinors $\{\chi_l^L\}$ and $\{\chi_s^S\}$ are constructed using the Dirac double group symmetry elements. χ_l^L and χ_s^S are defined by:

$$\chi_l^L = \begin{pmatrix} \chi_l^{L\alpha} \\ \chi_l^{L\beta} \\ 0 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_s^S = \begin{pmatrix} 0 \\ 0 \\ \chi_s^{S\alpha} \\ \chi_s^{S\beta} \end{pmatrix} \tag{7}$$

$$\chi_l^{L\alpha} = \sum_i g_i^L c_{il}^{L\alpha}, \quad \chi_l^{L\beta} = \sum_i g_i^L c_{il}^{L\beta}, \quad \chi_s^{S\alpha} = \sum_i g_i^S c_{is}^{S\alpha} \quad \text{and} \quad \chi_s^{S\beta} = \sum_i g_i^S c_{is}^{S\beta} \tag{8}$$

where coefficients $c_{ij}^{X\sigma}$ ($X \in \{L, S\}; \sigma \in \{\alpha, \beta\}$) in Eq. (8) are determined by symmetry. Thus, each non-zero component of these basis spinors consists of a linear combination of the basis functions from set $\{g_i^L\}$ or set $\{g_i^S\}$. This structure of the basis set is the only technical restriction on the choice of the basis spinors.

2.4 Kinetic balance and general contraction

Kinetic balance, discussed by several authors [16–18], is an important means to yield systematic improvement of the solutions upon basis set extension. This condition requires that for each four-spinor χ_l^L in the large component basis, the four-spinor $\alpha \cdot \boldsymbol{p}\chi_l^L$ is contained in the small component basis set. Since kinetic balance is neither a necessary nor sufficient condition to produce the best approximate eigensolutions, we normally extend the small component basis set beyond kinetic balance [17] (while maintaining the balance rigorously). In practice this means that the small component basis set contains more basis functions than those minimally required by the kinetic balance condition.

The small component basis set extension can consist of two types of additions. The first set of extra functions results from the fact that, where $\alpha \cdot \boldsymbol{p}$ operating on a single gaussian primitive in the large component yields a fixed linear combination of two gaussians in the small component, we still use these generated gaussians as two separate primitives instead of that fixed combination. Especially near the origin the kinetic balance condition is much too restrictive for the small component and this extension is an easy way to relax that restriction without violating the kinetic balance itself.

A second set of extra functions in the small component is used in molecular calculations where atomic solutions are used to contract the large and small component basis functions. When the contracted small component functions are derived by kinetic balance from the contracted large component functions, they differ significantly from the atomic small component solutions in the uncontracted basis set. Thus, in addition to the kinetically balanced functions the atomic small component solutions are used as small component basis functions. A basis set which includes such an extension is called an *atomically balanced* basis set.

When general contraction [19] is used to reduce the variational space we still require that the small component basis fulfils atomic and kinetic balance conditions. The contraction reduction is thereby somewhat counteracted by the fact that in some cases up to four contracted functions for each large component function are necessary: up to two functions to ensure kinetic balance, and up to two functions to ensure atomic balance. Although these small component functions together may become linear dependent for practical purposes (so that one or more functions may be removed) the gain by general contraction in the small component basis set is small compared to the gain in the large component basis set.

Using basis sets which have been constructed to fulfil the kinetic balance condition, we have not found any positive energy spurious solutions. Also, a lower bound to the total energy is not guaranteed by the use of such basis sets.

2.5 COSCI approach

For a number of applications a one-determinant approximation to the many-electron wavefunction is insufficient, even if electron correlation is not explicitly considered. For example if one wants to describe the ground state wavefunction of a carbon atom with its two $2p$ valence electrons using a one-determinant approximation, the closed shell would be a $2p_{1/2}{}^2$ configuration. But the carbon ${}^3P_0$ ground state is a mixture of the three $p_{1/2}{}^x - p_{3/2}{}^{2-x}$ $(x = 0, 1, 2)$ configurations. We handle this problem by constructing an average open shell energy expression [7] (with contributions from all possible determinants belonging to the configuration of interest, in this case p^2). Next the set of SCF spin-orbitals that belongs to the average expression is calculated. Using these 'average' spin-orbitals, the hamiltonian matrix is constructed in the complete open shell space and diagonalized. This procedure yields the stationary energies of all possible states from one configuration. Again for carbon, we get the energy for the ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, ${}^1D_0$ and ${}^1S_0$ states (all described with the same set of orbitals).

This method will be called the COSCI method (complete open shell configuration interaction); note that the orbitals are not optimized as in a CASSCF calculation. The COSCI method can be used within both the non-relativistic and the relativistic framework.

This example illustrates the need for the COSCI method to calculate the ground state of the atoms C to Pb. The results are used to calculate the binding energies of the hydrides.

Another important application of this method is the determination of the energy eigenvalue of the *f*-multiplet of rare-earch atoms in molecules or in solid state systems. Results from such calculations will be published shortly.

3 Applications

In this work, Hartree–Fock–Dirac calculations have been performed on the tetrahydrides XH_4, with X one of the atoms C, Si, Ge, Sn, or Pb. The bond length and binding energies are calculated for each of these molecules. To show the accuracy of the contracted basis sets used, some of the calculations have also been performed with the uncontracted basis set for comparison. The effect of the Breit interaction has also been studied.

To prepare for the molecular calculations, and for comparison with atomic calculations, we have performed separate Fock–Dirac calculations on H, C, Si, Ge, Sn, and Pb. For these atomic systems uncontracted basis sets can be used. The optimal atomic orbitals are used to construct (general) contracted basis sets for the hydride molecules.

3.1 Computational details

In Table 1 information on the basis sets relevant to the calculations on the systems described in this article are given. We use the notation $(ns, mp, \ldots \mid n's, m'p, \ldots)$ to indicate the number of primitive Gaussians used in the large and small component basis sets respectively. We use square brackets to describe the number of contracted functions.

Table 1. Summary of basis sets used in the calculations on XH_4 (NR: non-relativistic, FD: Fock–Dirac–(Beit))

XH_4	Basis for X	Basis for H	Remarks
CH_4	$(10s, 5p \mid 5s, 10p, 5d)$ $[8s, 4p \mid 5s, 10p, 5d]$	$(6s \mid 6p)$ $[4s \mid 6p]$	segmented contraction
SiH_4	$(12s, 8p \mid 8s, 12p, 8d)$ $[9s, 6p \mid 8s, 12p, 8d]$	$(6s \mid 6p)$ $[3s \mid 6p]$	segmented contraction
GeH_4	$(12s, 9p, 5d \mid 9s, 17p, 9d, 5f)$	$(6s \mid 6p)$	uncontracted
SnH_4	$(15s, 11p, 6d \mid 11s, 17p, 11d, 6f)$ $[11s, 9p, 5d \mid 10s, 13p, 10d, 5f]$	$(4s \mid 4p)$ $[3s \mid 3p]$	segmented contraction
PbH_4	$(19s, 16p, 10d, 5f \mid 16s, 19p, 16d, 10f, 5g)$ NR: $[7s, 6p, 3d, 1f]$ FD: $[7s, 10p, 6d, 2f \mid 13s, 18p, 16d, 8f, 4g]$	$(4s \mid 4p)$ $[2s \mid 2p]$	general contraction

Only for the PbH_4 molecule the *general* contraction scheme has been used. The primitive basis set was constructed from an existing non-relativistic basis set [20] which has been re-optimized under the constraint that the d-exponents form a subset of the s-exponents, and the f-exponents form a subset of the p-exponents. Using the relativistic atomic solution for the Pb-atom this basis was then contracted to a minimal atomic basis for the large component, with an extra diffuse s and p function to give flexibility in the valence region for Pb; for H one diffuse s-function has been added to the large component. The general contracted small-component basis was next constructed using both the atomic and kinetic balance conditions.

Details (list of primitive Gaussians and details of the segmented contractions) of the basis sets used for the calculations with X = C, Si, and Ge can be found elsewhere [5]. The primitive functions used in the contracted basis set for Sn can also be found elsewhere [5]; the contraction scheme we have used is available upon request.

The molecular calculations have been performed at the following X–H distances:

CH_4: $r = 1.07, 1.08, 1.09, 1.10, 1.11$ Å;

SiH_4: $r = 1.46, 1.47, 1.48, 1.49, 1.50, 1.51, 1.52$ Å;

GeH_4: $r = 1.48, 1.54, 1.56, 1.58, 1.64$ Å;

SnH_4: $r = 1.68, 1.72, 1.73, 1.74, 1.78$ Å;

PbH_4: $r = 0.988, 1.587, 1.693, 1.728, 1.737, 1.746, 1.799$ Å.

The bond lengths and force constants of these molecules have been determined by a parabolic fit using three points close to the minimum energy.

In most calculations, the Breit contribution to the total energy has been calculated using first order perturbation theory. For the GeH_4 molecule we have also performed calculations in which the Breit interaction was treated variationally. We have not included the Breit interaction in the COSCI calculations on the atoms; to get an estimate of the ground-state energies of the atoms including the Breit interaction we have used the Breit correction to the average SCF energy.

For the PbH_4 problem, two-electron integrals over small component basis functions with absolute numerical value less than 10^{-6} have not been used in order to reduce disk space. We have studied the possible effect of this approximation by setting the threshold further to 10^{-5}.

3.2 Results and discussion

3.2.1 Atomic results. The atomic results are collected in Table 2 and Fig. 1. The calculated values for the splittings within the ^3P terms show satisfactory agreement with experiment. For Ge, Sn and Pb the $^3P_2$-$^3P_0$ splitting differs from the experimental value by 3–9%, for the $^3P_1$-$^3P_0$ splitting the differences are 10–20%. Comparison with numerical results [21] shows that the differences with experiment are mainly due to the finite basis set approximation. The remaining error is due to the neglect of the Breit interaction and to the limited description by the COSCI approach.

If the Russell–Saunders coupling scheme is a good approximation of the wavefunction, and if the spin-orbit coupling is a small perturbation [22], the

Table 2. Atomic FD-COSCI results: Total energies, experimental results (from [23]), contributions of the $p_{1/2}{}^2$ and $p_{3/2}{}^2$ configurations to the ground state CI-vector. The contribution of a configuration to the ground state CI-vector has been calculated by summing the squares of the absolute value of the coefficients of all determinants belonging to the given configuration

Atom	$E_{tot}(^3P_0)$	$E(^3P_1)$-$E(^3P_0)$		$E(^3P_2)$-$E(^3P_0)$		$p_{1/2}{}^2$	$p_{3/2}{}^2$
	(a.u.)	(cm^{-1})	Exp(cm^{-1})	(cm^{-1})	Exp(cm^{-1})	(%)	(%)
C	−37.70287	19	16.4	57	43.5	66.8	33.2
Si	−289.47100	81	77.15	239	223.31	67.6	32.4
Ge	−2097.26431	507	557.10	1349	1409.90	71.4	28.6
Sn	−6174.94537	1357	1691.8	3111	3427.7	77.5	22.4
Pb	−20912.66788	6621	7819.35	10367	10650.47	92.1	8.0

splittings within the ^3P-level can be described using the Landé interval rule:

$$E_J - E_{J-1} = \lambda J \tag{9}$$

We observe a significant breakdown of the Landé interval rule for the heavier atoms. As usual, this can be explained by the deviation from LS coupling, which is evident from the contributions of the different configurations to the ground-state wavefunction, and by the fact that the Landé interval rule neglects all relativistic effects except spin-orbit coupling.

3.2.2 Molecular results. 3.2.2.1 Accuracy. The force constants are of course sensitive to the details of the fit used (the selection of the points taken in the fit). We estimate the absolute error in the force constants to be of the order of 10^{-2} a.u. The number of decimal places given in Table 5 is in accordance with this accuracy.

The non-relativistic calculations on PbH_4 with the uncontracted basis set predict a bond length $r_{min} = 1.80714$ Å, a binding energy for the molecule of $E_b = -0.28359$ a.u. and a force constant $k = 0.62$ a.u. If we compare these results given in Tables 3 to 5 (which have been obtained using general contracted basis sets) we find that the use of general contraction introduces a small error as a price for the loss of variational freedom: for the bond length a difference of

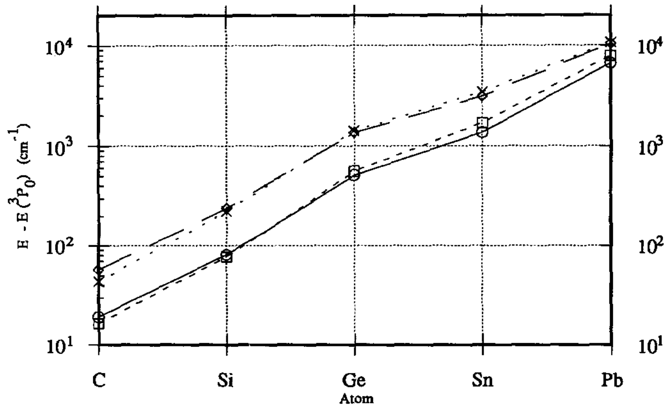

Fig. 1. Atomic FD-COSCI results for the $^3P_1$ and $^3P_2$ states relative to the $^3P_0$ states, compared with experiment [23].
—○— 3P1; —◇— 3P2; - -□- - 3P1 (exp.); · ·×· · 3P2 (exp.)

Table 3. Bond length r in Å (NR: non-relativistic, FD: Fock–Dirac, FD + BR: Fock–Dirac with Breit interaction included as a perturbation; Δr: difference with NR value)

	r (Å)			Δr (Å)	
Molecule	NR	FD	FD + BR	FD	FD + BR
CH_4	1.08327	1.08314	1.08323	−.00013	−.00004
SiH_4	1.48749	1.48660	1.48677	−.00089	−.00072
GeH_4	1.56379	1.55742	1.55793	−.00637	−.00586
SnH_4	1.75423	1.73280	1.73369	−.02143	−.02054
PbH_4	1.80772	1.73536	1.73703	−.07236	−.07069

Table 4. Binding energy E_b in a.u. (NR: non-relativistic, FD: Fock–Diract, FD + BR: Fock–Dirac and Breit interaction included as a perturbation; ΔE_b: difference with NR value

	E_b (a.u.)			ΔE_b (a.u.)	
Molecule	NR	FD	FD + BR	FD	FD + BR
CH_4	−.50423	−.50371	−.50361	.00052	.00062
SiH_4	−.35645	−.35446	−.35436	.00199	.00209
GeH_4	−.32177	−.30814	−.30805	.01363	.01372
SnH_4	−.28108	−.25144	−.25131	.02964	.02977
PbH_4	−.27643	−.18948	−.18867	.08695	.08776

Table 5. Force constant k in a.u. (NR: non-relativistic, FD: Fock–Dirac, FD + BR: Fock–Diract with Breit interaction included as a perturbation; Δk: difference with NR value)

	k (a.u.)			Δk (a.u.)	
Molecule	NR	FD	FD + BR	FD	FD + BR
CH_4	1.52	1.52	1.52	−0.00	−0.00
SiH_4	0.82	0.80	0.81	−0.01	−0.01
GeH_4	0.67	0.65	0.66	−0.02	−0.02
SnH_4	0.53	0.53	0.53	0.00	0.00
PbH_4	0,61	0.62	0.61	0.01	−0.01

6×10^{-4} Å is found and for the binding energy a difference of 7×10^{-3} a.u. is found (the force constant did not change significantly).

The results of the Fock–Dirac calculations on PbH_4 in which the small-component two-electron integrals with absolute value less than 10^{-5} have been ignored ($r_{min} = 1.73535$ Å, $E_b = -0.18948$ a.u., $k = 0.62$ a.u.) show (by comparison with the data in the tables) that the error introduced by leaving out those small integrals is not significant.

In Tables 3 and 4 we have given five decimal places in order to see the differences introduced by the Breit correction. We expect that the calculated bond length for PbH_4 will be accurate in three decimal places. The binding energies for PbH_4 have an estimated error of the order of 10^{-2} a.u. For the other molecules, the results will be significantly more accurate since the basis sets used to produce those results have not been as heavily contracted as the basis sets used for the PbH_4 calculations. Basis set truncation errors (and errors from leaving out functions with higher angular momentum) have not been estimated.

3.2.2.2 Hartree–Fock–Dirac results. The Hartree–Fock–Dirac results show the well-known relative relativistic bond length contraction; we find relativistic contractions ranging from 0.01% (CH_4) to 4.2% (PbH_4). This leads to a bond length of the Pb–H bond in the PbH_4 molecule which is very close to the Sn–H bond length in SnH_4.

The Hartree–Fock–Dirac results also show that, going from the lighter to the heavier systems, the binding energy decreases significantly in absolute value. This results in a binding energy of PbH_4 which is significantly smaller than the binding energy of SnH_4 (the non-relativistic theory predicts that both binding energies are about equal).

We also find a small decrease in the force constants of the Si–H and Ge–H bonds. For the other molecules the differences between the force constants calculated by the Hartree–Fock–Dirac method and by the non-relativistic method are not significant.

3.2.2.3 Effect of the Breit interaction. In Fig. 2 the bond length found by the relativistic calculations (with and without the Breit interaction) is given relative to the bond length predicted by non-relativistic calculations. It can be seen that for PbH_4 the Breit interaction leads to a slightly longer bond length; for the other molecules the absolute effect is small. The data in Table 3 show the general trend that the effect of the Breit interaction forms a large part of the relativistic effects on the bond length for the lighter systems.

Thus, for the heavy systems the effect of the Breit interaction should be taken into account (although correlation corrections are expected to be much more important), while for the lighter systems the Breit interaction should be included when relativistic effects are considered (in CH_4, the Breit interaction cancels a large part of the bond length contraction found neglecting the Breit interaction).

The binding energy and the force constants are also influenced by the Breit interaction, but in general no significant deviations from the Dirac–Coulomb results are found.

In Fig. 3 the total SCF-energy and the Breit correction to this energy as a function of the bond length are shown for the PbH_4 molecule. In the bond length region we have examined, we find that the Breit interaction gets less positive with increasing bond length. The Breit interaction thus favours bond length expansion (relative to the bond length predicted by a relativistic calculation without the Breit interaction). The slope of the Breit correction versus the bond length is very

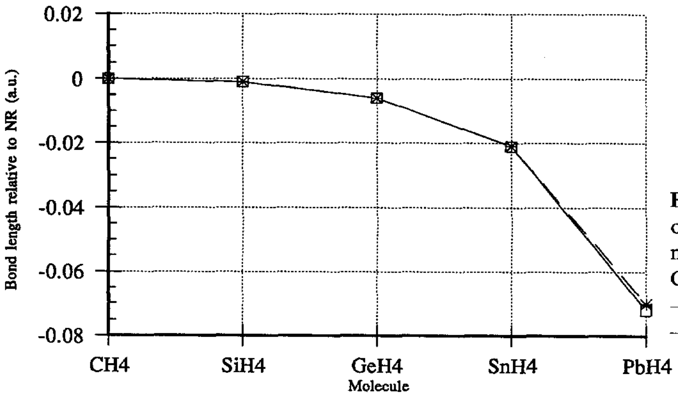

Fig. 2. Relativistic effect on the bond length of the molecules XH_4, X = C, Si, Ge, Sn, and Pb.
—□— Fock–Dirac;
—*— Fock–Dirac–Breit

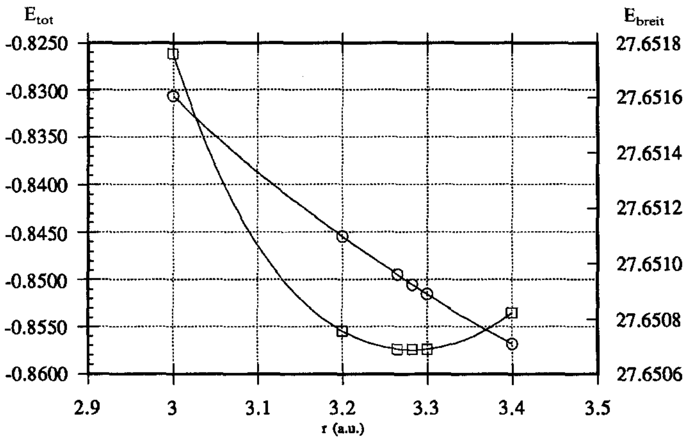

Fig. 3. Total energy and Breit correction for PbH_4 as a function of the bond length r. □ E_{tot} (+20914 a.u.); ○ E_{breit} (a.u.)

small (relative to the depth of the well provided by the total SCF-energy versus the bond distance), so the resulting bond length expansion is also very small.

For the GeH_4 molecule, we have also performed some calculations treating the Breit interaction variationally. The bond length and the force constant obtained by these calculations are identical to the results given in the tables; for the binding energy we find a difference of 6×10^{-4} a.u., which is not significant. Thus we conclude that for lighter systems, as far as bond lengths, force constants and bond energies are concerned, it makes no difference whether the Breit interaction is treated as a perturbation or it is treated variationally.

3.2.2.4 Comparison with other methods. In Table 6 some theoretical and experimental results which have been given by other authors are presented. This list was largely compiled using data given by Pyykkö [1]. In the various results, different methods and basis sets have been used. Although therefore care must be taken when extracting general trends from these data we can make some points.

First of all, it is evident that the one-component relativistic one-center $X_{\alpha\beta}$ method used by Aguilar-Ancono et al. significantly overestimates the bond lengths of the systems considered. The DF-OCE method used by Desclaux and Pyykkö also overestimates bond lengths. This is almost certainly a defect of the one-center expansion technique. The other data essentially give the same figures for the molecules other than PbH_4. For PbH_4, perturbation theory overestimates the bond length contraction quite a lot, while the results from the pseudopotential methods are close to our results but do not show a systematic trend.

After completion of this work we received a report from Dyall, Taylor, Faegri, and Partridge in which they describe results of Dirac–Hartree–Fock calculations on the series CH_4 to PbH_4. The main differences between the method described in this work and the method used by Dyall et al. are the choice of the small component basis sets and the inclusion of the Breit interaction (Dyall et al. have not included the Breit interaction). Nevertheless, their results are in close agreement with our results.

The experimental figures in the table show that there is still a significant discrepancy between the theoretical and experimental numbers. This illustrates the fact that, except for the lighter elements, relativistic effects are equally, but not more important than correlation effects. It is interesting to see that for PbH_4 the relativistic effects are much more important than the correlation effects

Table 6. Bond length results from listerature. The 'experimental' value for PbH_4 was deduced (following Desclaux and Pyykkö) from $r(PbH_4) = r(PbH) + r(SnH_4) - r(SnH)$

XH_4	r_{NR} (Å)	r_{Rel} (Å)	Δr (Å)	Method, reference
CH_4		1.083	0.00010	P-HF Almlof and Faegri [24]
CH_4	1.099	1.099	0.000	DF-OCE Desclaux and Pyykkö [26]
CH_4		1.145		X_α Aguilar-Ancono, Gázquez and Keller [27]
CH_4	1.0833	1.0832	0.00004	FD + BR This work
CH_4		1.086		Experiment [25]
SiH_4		1.482	0.00066	P-HF Almlof and Faegri [24]
SiH_4		1.572	0.001	DF-OCE Desclaux and Pyykkö [26]
SiH_4		1.586		X_α Aguilar-Ancono, Gázquez and Keller [27]
SiH_4	1.4875	1.4868	0.0007	FD + BR This work
SiH_4		1.481		Experiment (taken from Desclaux and Pyykkö [26])
GeH_4		1.521	0.0070	P-HF Almlof and Faegri [24]
GeH_4	1.596	1.586	0.010	DF-OCE Desclaux and Pyykkö [26]
GeH_4		1.603		X_α Aguilar-Ancono, Gázquez and Keller [27]
GeH_4		1.522		PP-MRCI Das and Balasubramanian [31]
GeH_4	1.564	1.558	0.0059	FD + BR This work
GeH_4		1.527		Experiment (taken from Desclaux and Pyykkö [26])
SnH_4		1.705	0.021	P-HF Almlof and Faegri [24]
SnH_4	1.804	1.772	0.032	DF-OCE Desclaux and Pyykkö [26]
SnH_4		1.783		X_α Aguilar-Ancono, Gázquez and Keller [27]
SnH_4	1.732	1.715	0.017	PP-HF Pélissier [28]
SnH_4	1.736	1.717	0.019	PP-HF Fernandez, Arriau and Dargelos [29]
SnH_4	1.754	1.734	0.0205	FD + BR This work
SnH_4		1.701		Experiment (taken from Desclaux and Pyykkö [26])
PbH_4		1.703	0.10	P-HF Almlof and Faegri [24]
PbH_4	1.89	1.782	0.107	DF-OCE Desclaux and Pyykkö [26]
PbH_4	1.827	1.743	0.084	PP-HF Pélissier [28]
PbH_4		1.795		X_α Aguilar-Ancono, Gázquez and Keller [27]
PbH_4	1.806	1.732	0.074	ARPP Schwerdtfeger, Silberbach, Miehlich [30]
PbH_4	1.806	1.739	0.067	QRPP Schwerdtfeger, Silberbach, Miehlich [30]
PbH_4	1.808	1.737	0.0707	FD + BR This work
PbH_4		1.754		'Experiment' (from Desclaux and Pyykkö [26])

r_{NR}: non-relativistic bond length; r_{Rel}: relativistic bond length; Δr: difference between r_{NR} and r_{Rel}; P-HF: Perturbation theory; PP-HF: Pseudopotential Hartree–Fock; PP-MRCI: Pseudopotential Multireference CI; X_α: one-component relativistic method with $X_{\alpha\beta}$ local exchange, using a spherical symmetric one-center approximation; ARPP: spin-orbit averaged relativistic pseudopotential; QRPP: spin-orbit coupled pseudopotential (quasi relativistic pseudopotential); DF-OCE: Dirac–Fock one center expansion; FD + BR: Fock–Dirac with Breit interaction included as a perturbation

(assuming these effects to be largely additive and the quoted 'experimental' value to have sufficient significance). This is particularly well illustrated by the results of Almlof and Faegri [24], who are generally right on target with their perturbative approach except where the relativistic effects are becoming dominant, as is the case for Pb and PbH_4.

4 Conclusions

In this article we have given results which show the state of the art in *ab initio* molecular relativistic quantum-chemical calculations using the Fock–Dirac–

(Breit) formalism. The general contraction method introduced in this context, using kinetic and atomic balance for the small components of molecular basis sets, contributes to the feasibility of reliable relativistic *ab initio* methods.

In our calculations on the hydrides, we have verified that the Breit interaction leads to small but sometimes significant corrections to the relativistic results both for light and heavy atoms (bond length expansion for the PbH_4). For the lighter systems the Hartree-Fock-Dirac method without the Breit interaction overestimates the bond length contractions (for CH_4 by about a factor 3). We have also found that the relativistic effects are much more important than the correlation effects for the PbH_4 molecule and are therefore to be taken into account first.

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