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Calculations of the indirect nuclear spin–spin coupling constants of PbH_4

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Abstract. We report ab initio calculations of the indirect nuclear spin–spin coupling constants of PbH_4 using a basis set which was specially optimized for correlated calculations of spin–spin coupling constants. All nonrelativistic contributions and the most important part of the spin–orbit correction were evaluated at the level of the random phase approximation. Electron correlation corrections to the coupling constants were calculated with the multiconfigurational linear-response method using extended complete and restricted active space wavefunctions as well as with the second-order polarization propagator approximation and the second-order polarization propagator approximation with coupled-cluster singles and doubles amplitudes. The effects of nuclear motion were investigated by calculating the coupling constants as a function of the totally symmetric stretching coordinate. We find that the Fermi contact term dominates the Pb—H coupling, whereas for the H—H coupling it is not more important than the orbital paramagnetic and diamagnetic contributions. Correlation affects mainly the Fermi contact term. Its contribution to the one-bond coupling constant is reduced by correlation, independent of the method used; however, the different correlated methods give ambiguous results for the Fermi contact contribution to the H—H couplings. The dependence of both coupling constants on the Pb—H bond length is dominated by the change in the Fermi contact term. The geometry dependence is, however, overestimated in the random phase approximation.

Key words: PbH_4 – NMR parameters – Spin–spin coupling constants – Basis set – Multiconfigurational linear response

1 Introduction

In four previous publications [1–4] correlated calculations of the indirect nuclear spin–spin coupling constants of the fourth main-group hydrides, CH_4, SiH_4, GeH_4, and SnH_4, were reported. The results included the random phase approximation (RPA) [1–3], the multiconfigurational linear-response (MCLR) method [1–3], the second-order polarization propagator approximation (SOPPA) [3], and SOPPA with coupled-cluster singles and doubles amplitudes SOPPA(CCSD) calculations [4] of all four contributions to the coupling constants. In addition, spin–orbit corrections were calculated at the RPA level [2] and first-order estimates of ro–vibrational corrected and zero-point vibrational averaged (ZPVA) values of the coupling constants were evaluated at the RPA, MCLR, and SOPPA levels of approximation [3]. In the case of CH_4 second-order estimates of the ro–vibrational corrections to the coupling constants were also calculated at the SOPPA(CCSD) level [4].

It was found that correlation effects are large for the Fermi contact (FC) and spin-dipolar (SD) terms, smaller but usually not negligible for the orbital paramagnetic (OP) contributions, and insignificant for the orbital diamagnetic (OD) terms. The spin dipolar contributions to both the one- and two-bond coupling constants of CH_4, SiH_4, GeH_4, and SnH_4 were very small, which rendered their sensitivity to electron correlation unimportant. The spin–orbit corrections turned out to be small, amounting at most to only 1% for ${}^1J_{\mathrm{Sn—H}}$ in SnH_4. The ZPVA corrections dominated the ro–vibrational contributions and are at least as large as the noncontact contributions to the one-bond couplings and even more important for the H—H couplings. Thus, if experimental accuracy is desired inclusion of nuclear motion effects is mandatory.

As also observed by others [5, 6], calculations of geminal proton–proton coupling constants are a challenging problem, as satisfactory agreement with experimental results is often difficult to obtain. This can partly be explained by the large basis set and correlation sensitivity usually exhibited by H—H couplings. One-bond couplings show similar sensitivity, although to a much lesser degree.

The purpose of the present study is to establish the nonrelativistic limit for the indirect nuclear spin–spin coupling constants of PbH_4 and to estimate the size of the nuclear motion and spin–orbit corrections.

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Pb is heavy and one cannot expect agreement with experiment without a proper treatment of the relativistic effects. There are several ways in which one may include them. The proper way would be a correlated relativistic four-component linear-response calculation. Since to our knowledge such a method has not yet been implemented, we chose a perturbation theory approach based on a Pauli-type Hamiltonian; however, due to the unboundedness of the mass velocity and Darwin operators, only the spin–orbit operator was used as in the previous study of CH_4, SiH_4, GeH_4, and SnH_4 [2]. One might ask whether such a perturbation theory approach is valid for calculations of the relativistic corrections to nuclear spin–spin coupling constants involving Pb. Apart from the study on CH_4, SiH_4, GeH_4, and SnH_4 [2], where this question was discussed in more detail, we are not aware of any other previous attempt to calculate spin–orbit corrections to spin–spin coupling constants; however, relativistic corrections to polarizabilities have for example, been frequently calculated using a perturbation theory approach with the mass velocity and Darwin operators (see, e.g. Ref. [7]). Comparison with the Douglas–Kroll approximation showed that this approach works very well for elements of the fourth and fifth period, whereas larger deviations were observed for elements of the sixth period [7]. Furthermore Nakatsuji and coworkers [8–12], and Vaara et al. [13] have calculated relativistic corrections to the nuclear magnetic shielding tensor, a property closely related to the indirect nuclear spin–spin coupling constants. Whereas Vaara et al. calculated the spin–orbit corrections from quadratic response functions as in our work, Nakatsuji and coworkers calculated not only the spin–orbit corrections, but also investigated the effect of the scalar mass velocity and Darwin corrections by using the spin-free Douglas–Kroll approximation. In their studies of several mercury [9] and tungsten [11] compounds they found good agreement with experiment on inclusion of these relativistic corrections; however, they noticed that, although the spin–orbit corrections are important, the scalar corrections are larger and that there is a significant coupling between them. Therefore, we are not able to predict the total relativistic correction to the coupling constants as would be included in a corresponding relativistic four-component linear-response calculation [14], but our results can give an indication of the size of the spin–orbit effects.

Besides, in view of, for example, semi-empirical calculations [15] or future ab initio relativistic four-component calculations [14] it is necessary to establish the ab initio nonrelativistic limit for the spin–spin coupling constants, since only in comparision with the proper nonrelativistic limit can the relativistic effects be quantified.

2 Methods

The four contributions to the isotropic part of the indirect nuclear spin–spin coupling constant, first derived by Ramsey [16], are the OP term

$$J_{KL}^{\mathrm{OP}} = \frac{2}{3}\sum_{\alpha=x,y,z}\left(\frac{\mu_0}{4\pi}\right)^2\left(\frac{e\hbar}{m_\mathrm{e}}\right)^2\frac{\gamma_K\gamma_L}{h} \times \sum_{n\neq 0}\frac{\langle 0 \mid \sum_i \frac{(\mathbf{l}_{iK})_\alpha}{r_{iK}^3} \mid n\rangle\langle n \mid \sum_i \frac{(\mathbf{l}_{iL})_\alpha}{r_{iL}^3} \mid 0\rangle}{E_0 - E_n}\ , \tag{1}$$

the FC term

$$J_{KL}^{\mathrm{FC}} = \frac{2}{3}\sum_{\alpha=x,y,z}\left(\frac{\mu_0}{4\pi}\right)^2\left(\frac{4\pi g_\mathrm{e} e\hbar}{3m_\mathrm{e}}\right)^2\frac{\gamma_K\gamma_L}{h} \times \sum_{n\neq 0}\frac{\langle 0 \mid \sum_i (\mathbf{s}_i)_\alpha \delta(\mathbf{r}_{iK}) \mid n\rangle\langle n \mid \sum_i (\mathbf{s}_i)_\alpha \delta(\mathbf{r}_{iL}) \mid 0\rangle}{E_0 - E_n}\ , \tag{2}$$

the SD term

$$J_{KL}^{\mathrm{SD}} = \frac{2}{3}\sum_{\alpha=x,y,z}\left(\frac{\mu_0}{4\pi}\right)^2\left(\frac{g_\mathrm{e} e\hbar}{2m_\mathrm{e}}\right)^2\frac{\gamma_K\gamma_L}{h} \times \sum_{n\neq 0}\frac{\langle 0 \mid (\mathbf{O}_K^{\mathrm{SD}})_\alpha \mid n\rangle\langle n \mid (\mathbf{O}_L^{\mathrm{SD}})_\alpha \mid 0\rangle}{E_0 - E_n}\ , \tag{3}$$

with

$$(\mathbf{O}_K^{\mathrm{SD}})_\alpha = \sum_i \frac{3(\mathbf{s}_i \cdot \mathbf{r}_{iK})(\mathbf{r}_{iK})_\alpha - r_{iK}^2(\mathbf{s}_i)_\alpha}{r_{iK}^5}\ , \tag{4}$$

and the OD term

$$J_{KL}^{\mathrm{OD}} = \frac{1}{3}\sum_{\alpha=x,y,z}\left(\frac{\mu_0}{4\pi}\right)^2\frac{e^2\hbar^2}{m_\mathrm{e}}\frac{\gamma_K\gamma_L}{h} \times \langle 0 \mid \sum_i \left(\frac{\mathbf{r}_{iL}\cdot\mathbf{r}_{iK} - (\mathbf{r}_{iL})_\alpha(\mathbf{r}_{iK})_\alpha}{r_{iL}^3 r_{iK}^3}\right) \mid 0\rangle\ , \tag{5}$$

where $\mathbf{r}_{iK}$, $\mathbf{l}_{iK}$, and $\mathbf{s}_i$ are the position vector of electron i relative to nucleus K, the angular momentum operator of electron i defined with nucleus K as the origin, and the electron spin operator of electron i respectively. Note that orbital as well as the spin angular momentum operators, $\mathbf{l}_{iK}$ and $\mathbf{s}_i$, have SI units (Js). The OP, FC, and SD terms consist of sums over all excited electronic states $\mid n\rangle$ with energies E_n and $|0\rangle$, E_0 refer to the electronic ground state. The magnetogyric ratios of nucleus K and L are denoted by γ_K and γ_L, respectively. All the other symbols have their usual meaning [17]. Sum-over-states expressions as Eqs. (1)–(3) are linear-response functions, whereas the OD term (Eq. 5) is a ground-state average value, although it can be reformulated as a sum-over-states expression [18].

Due to the δ function in the FC contribution relativistic effects are expected to be largest for this term. This was confirmed by the calculations of spin–orbit corrections to the coupling constants of XH_4, X = C, Si, Ge, and Sn (see Ref. [2], where the method for obtaining these corrections is also described in detail). Suffice it to say that the spin–orbit corrections introduce four non-zero cross-term contributions to the isotropic part of the coupling constant, of which we calculated two, namely the OP–FC and the OP–SD cross terms. In a previous study it was concluded that inclusion of the OP–FC cross term is sufficient to get a reliable estimate of the spin–orbit effects. In view of the computational effort required to calculate the relatively unimportant OP–SD cross term, we have chosen to omit it in the present investigation. Further, since the one-electron spin–orbit contribution turned out to dominate and has the opposite sign to the two-electron contribution, it is possible to assess the importance of the total spin–orbit correction by calculating only the one-electron correction. The validity of this approximation is, in particular for PbH_4, further supported by the fact that the ratio of the one-electron to the two-electron correction decreases from CH_4 to SnH_4 in the XH_4 series. Therefore, we have only included the one-electron spin–orbit correction to the OP–FC cross term.

Previous investigations [3, 4] of the ZPVA corrections to the indirect nuclear spin–spin coupling constants in the XH_4 series showed that agreement with experiment cannot be expected without inclusion of ro–vibrational effects. In the present study we estimated the effect of nuclear motion by calculating the coupling constants for six different values of the totally symmetric stretching coordinate, since this is the only normal coordinate that contributes to the ro–vibrational averaging of the coupling constants in first order.

3 Computational details

All calculations were performed with a version of the DALTON program package [19, 20], whose property module ABACUS had been modified to perform SOPPA [21] and SOPPA(CCSD) calculations [22] of indirect nuclear spin–spin coupling constants, except for the calculation of the CCSD amplitudes used in SOPPA(CCSD), which were obtained from the integral-direct coupled-cluster program of Koch and coworkers [23, 24]. The Pb—H distance was set to 1.74200 Å, which is close to the estimated Dirac–Hartree–Fock value [25].

3.1 Basis set

The basis set was carefully optimized for correlated calculations of spin–spin coupling constants. We started with the $(20s16p11d7f)/[8s7p5d1f]$ basis for Pb used by Dyall et al. [25], and the $(9s2p)/[6s2p]$ basis for H [26], which was used in the previous calculations of coupling constants of the XH_4 series [1–4].

At first, each shell (s, p, d, f) of the Pb basis was decontracted separately to find the maximum obtainable effect on the coupling constants at the RPA and valence complete active spare (CAS) MCLR level. Subsequently, we tried to reproduce these changes to 1% or less by only partially decontracting the different shells. This procedure converged fast for the Pb—H coupling constant. Converging the H—H coupling constant required a larger degree of decontraction. Furthermore, a convergence to 1% was not possible, since the H—H coupling is small, between 0.5 Hz and 6 Hz depending on the basis and correlation level. We therefore estimate the remaining basis set error on the H—H couplings to be about 0.5 Hz due to lack of complete decontraction. In addition, the Pb basis set was augmented in each set with compact and tight functions until the change was less than 1% in $^{1}J_{\mathrm{Pb-H}}$ and less than 0.5 Hz for $^{2}J_{\mathrm{H-H}}$. Finally, polarization functions (g functions) were added to the Pb basis set. Since the sensitivity of the one-bond and two-bond coupling constants to the exponents of the polarization functions turned out to be different, we added three g functions with exponents 2, 0.5, and 0.125. The RPA and MCLR calculations did not show a significantly different dependence of the coupling constants on the variation of the basis set. This was true also for the polarization functions, where one might expect a different behavior of correlated and uncorrelated methods to show up. Details of the final $(22s16p12d10f3g)/[22s12p9d8f3g]$ Pb basis set are given in Tables 1 and 2.

Although the basis set for H was optimized [26] for coupling constants, it was done for the H—H and C—H couplings in CH_4; therefore, we decided to test if decontraction of the s space in the H basis set would have any influence on the coupling constants in PbH_4. It turned out that only the FC contribution to both the $^{1}J_{\mathrm{Pb-H}}$ and $^{2}J_{\mathrm{H-H}}$ couplings was altered; however, the changes were insignificant.

3.2 Correlated calculations

Correlation was included in two ways.

1. Using the MCLR method with CAS or restricted active space (RAS) self-consistent-field wavefunctions as reference states and different active spaces.

Table 1. Exponents and contraction coefficients of the s- and p-type functions in the Gaussian basis set for Pb

Shell	Exponent	Shell	Exponent	Contraction coefficients			
s	104324642	p	65535.5043	0.00028	0.00014	0.00007	0.00003
	15626093.5		15525.3525	0.002481	0.001259	0.000631	0.0002622
	2340528.5		5038.94022	0.0138384	0.00711	0.003548	0.0014845
	532657.386		1923.64983	0.0565741	0.029784	0.0150502	0.00626954
	150859.596		813.959465	0.170262	0.0944408	0.0479719	0.0201683
	49208.5357		369.158709	0.34672	0.207595	0.108663	0.0455253
	17762.3608		175.784307	0.392675	0.237925	0.122259	0.052112
	6928.27349		85.8307392	0.175014	−0.109194	−0.0962798	−0.0469728
	2876.44261		42.9163904				
	1259.68999		21.7911795				
	575.46689		10.2692843				
	228.552035		5.0168962				
	107.322499		1.96183081				
	44.330316		0.82495938				
	23.7415742		0.198292989				
	9.87476487		0.0653737				
	5.1346173						
	1.68025397						
	0.822037005						
	0.172238915						
	0.067542142						
	0.02648612						

2. Employing linear-response methods based on Møller–Plesset perturbation theory, here SOPPA and SOPPA(CCSD).

The first method includes what is normally denoted static correlation, although some dynamical correlation is incorporated when large active spaces are employed. The second approach, on the other hand, takes into account only dynamical correlation. Details of CAS and RAS [27, 28] multiconfigurational self-consistent-field (MCSCF) wavefunctions, the MCLR [29, 30], SOPPA [31] and SOPPA(CCSD) [22] methods are given elsewhere.

The active spaces used in the MCLR calculations are given in Table 3. The first, CAS A, is a valence CAS (6*s*, 6*p* on Pb and 1*s* on each H), which includes eight electrons in eight orbitals resulting in 1252 determinants in D_2 symmetry. In CAS B we have, guided by the MP2 natural occupation numbers [32], included the 5*d* shell on Pb; thus, in the active space CAS B has 18 electrons distributed in 13 orbitals, giving 127975 determinants. It may be regarded as an extended valence CAS including the outer core (next to valence) 5*d* orbitals. In CAS C, the active space includes more virtual orbitals than in CAS A, whose selection was based on the MP2 natural occupation numbers. The resulting CAS C active space with eight electrons in 20 orbitals is shown in Table 3.

The next obvious step (CAS D) would be a CAS calculation embracing the active spaces of both CAS B and CAS C; however, this calculation with 18 electrons in 25 orbitals, is computationally not feasible. A compromise is to perform a RAS calculation containing the same orbitals. There are many ways of choosing the subspaces for RAS calculations. In all the RAS calculations presented here, the active space of the corresponding CAS wavefunction was divided such that RAS I contained the occupied orbitals (with respect to Hartree–Fock), RAS II was kept empty and RAS III consisted of the virtual orbitals. All singles and doubles excitations from RAS I into RAS III are then allowed, which corresponds to a restricted singles and doubles configuration interaction with optimization of the orbitals. Thus RAS D consists of the 5*d*, 6*s*, and 6*p* orbitals on Pb in RAS I and 16 virtual orbitals in RAS III, namely 6*s*′, 6*p*′, 5*d*′, and 5*f*; however, this choice for the active space made the variational procedure replace the 6*s* with the 5*s* orbital, and hence correlates the valence shell incompletely. The same behavior was observed in our previous calculations on SnH_4 [1]; therefore, we concluded that it was also necessary to include the 5*s* and 5*p* orbitals in the active space in addition to further correlating *s* and *p* orbitals leading to 26 electrons in 33 orbitals. The size of this active space allows only a RAS calculation, denoted RAS E, with 24531 determinants.

Table 2. Exponents and contraction coefficients of the d-, f- and g-type functions in the Gaussian basis set for Pb

Shell	Exponent	Contraction coefficients			Shell	Exponent	Contraction coefficients	Shell	Exponent
d	2487.69723	0.00245082	0.00129181	0.00045156	f	346.477152	0.00456457	g	2
	751.579185	0.0217528	0.0114801	0.00403076		119.83564	0.0361271		0.5
	290.91448	0.102737	0.0558934	0.0196645		50.2301342	0.139312		0.125
	126.825859	0.287911	0.158653	0.0562038		22.8305181			
	58.8017533	0.442575	0.234055	0.0815415		10.5504129			
	28.2408638	0.293941	−0.0111774	−0.0189844		4.78302212			
	13.186762					1.96486696			
	6.08313907					0.80716795			
	2.53113912					0.33158484			
	1.05169578					0.13621514			
	0.386102157								
	0.15444								

Table 3. Active spaces employed in the complete active space (*CAS*) and restricted active space (*RAS*) self-consistent-field (*SCF*) calculations

MCSCF	No. of electrons	No. of orbitals	Active space	No. of determinants
CAS A	8	8	7–8a_1,9–10t_2	1252
CAS B	18	13	7–8a_1,3e,8–10t_2	127975
CAS C	8	20	7–9a_1,4e,9–12t_2,2t_1	5870025
CAS D	18	25	7–9a_1,3–4e,8–12t_2,2t_1 (not done)	–
CAS E	26	33	6–10a_1,3–4e,7–13t_2,2t_1 (not done)	–
RAS A[a]	8	8	7a_1,9t_2 (RASI) 8a_1,10t_2 (RASIII)	97
RAS B[a]	18	13	7a_1,3e,8–9t_2 (RASI) 8a_1,10t_2 (RASIII)	463
RAS C[a]	8	20	7a_1,9t_2 (RASI) 8–9a_1,4e,10–12t_2,2t_1 (RASIII)	1441
RAS D[a,b]	18	25	7a_1,3e,8–9t_2 (RASI) 8–9a_1,4e,10–12t_2,2t_1 (RASIII)	7465
RAS E[a]	26	33	6–7a_1,3e,7–9t_2 (RASI) 8–10a_1,4e,10–13t_2,2t_1 (RASIII)	24531

[a] Same active space as the corresponding CAS. Single and double excitations from RAS I to RAS III

[b] Correlates erroneously the inner valence orbitals

In addition, similar RAS calculations corresponding to CAS A, CAS B, and CAS C were carried out. From the differences between these CAS and RAS calculations and from the results obtained with RAS E one can estimate what the result of a calculation with CAS E would be.

4 Results

4.1 Correlation and spin–orbit corrections to the coupling constants

The results for the four nonrelativistic (FC, SD, OP, OD) contributions and the one-electron part of the FC–OP spin–orbit correction to the $^1J_{\mathrm{Pb-H}}$ coupling constant obtained with the different methods are given in Table 4. Most striking is the complete dominance of the FC term. The only other significant term is the relativistic spin–orbit correction, which estimated from the one-electron part of the FC–OP cross term amounts to about 10% of the FC term at the RPA level. The other three nonrelativistic contributions to $^1J_{\mathrm{Pb-H}}$ are less than 1% of the FC contribution. Since the SD contribution is unimportant and computationally very expensive, we calculated this term only at the RPA level and for the valence CAS (CAS A).

The FC contribution to the Pb—H coupling constant exhibits the usual strong correlation dependence (between 14 and 26%), almost independent of how correlation is treated. The FC terms obtained with RAS B and RAS C, which only include single and double excitations, differ by less than 1% from the corresponding CAS B and CAS C results indicating that the effect of higher excitations is negligible, in agreement with our previous results [1]. We therefore expect the RAS E results to be accurate estimates of the corresponding CAS E values. Analyzing the data in more detail, we note that the valence CAS (CAS A) result is almost 400 Hz smaller than the RPA result. Inclusion of the inner valence, 5*d*, orbitals (CAS B/RAS B) does not significantly change this, whereas inclusion of virtual orbitals (CAS C/RAS B) reduces the FC term by an additional 94 Hz; however, combination of these two active spaces and inclusion of the inner valence 5*s* and 5*p* orbitals together with the corresponding correlating orbitals in RAS E again leads to an increase in the FC term. The two perturbation-based methods, SOPPA and SOPPA(CCSD), give results for $^1J_{\mathrm{Pb—H}}$ close to CAS A and CAS C, respectively. Most of the correlation contribution to $^1J_{\mathrm{Pb—H}}$ can thus be found using a valence CAS or SOPPA, which give the same sign and approximately the same magnitude, similar to what was found for the $J(\mathrm{X—H})$ coupling constants of the other molecules in the $\mathrm{XH_4}$ series [3]. From a comparison of the RPA and CAS A results, the SD term can be seen to be very sensitive to correlation; however its small size makes this fact unimportant. The remaining two terms, OP and OD, are slightly affected by correlation.

The situation is quite different for the geminal proton–proton coupling constants $^2J_{\mathrm{H—H}}$ shown in Table 5. First, the FC, OP, and OD terms are all of the same order of magnitude. The SD term and the relativistic spin–orbit correction, estimated from the one-electron part of the FC–OP cross term at the RPA level, are much smaller, although their contribution to the total $^2J_{\mathrm{H—H}}$ coupling constant is somewhat larger due to the near cancellation of the three main terms. The SD contribution was thus only calculated at the RPA and CAS A level.

Secondly, the FC contribution to $^2J_{\mathrm{H—H}}$ is much more sensitive to correlation effects and whether perturbation-theory-based or variational methods are used to treat correlation. The valence CAS (CAS A) reduces the FC term to about 12% of its RPA value. Inclusion of the inner valence 5*d* orbitals in CAS B and RAS B leads to an increase in the FC term again, although it is still smaller than at the RPA level; however, CAS C and RAS C, which include more virtual orbitals than CAS A, predict the FC term to be 50% larger than its RPA value. RAS E, which is a combination of the active spaces of RAS B and C and contains additional inner valence (5*s*, 5*p*) and correlating orbitals, gives almost the same result as CAS C and RAS C. As for the $^1J_{\mathrm{Pb—H}}$ coupling constants, the differences between the CAS and corresponding RAS calculations are so small that it is safe to expect the CAS E results to be only insignificantly different from the RAS E values. The two perturbation-theory-based methods, SOPPA and SOPPA(CCSD), on the other hand increase the FC term by more than a factor of 4. This is consistent with results for the geminal coupling constants of $\mathrm{SiH_4}$, $\mathrm{GeH_4}$, and $\mathrm{SnH_4}$, where for a given X-H distance the $^2J_{\mathrm{H—H}}$ couplings obtained with SOPPA are markedly larger than those obtained from the RPA or any MCLR calculation [3]. Finally, the SD contribution as well as the other two

Table 4. One-bond, $^1J_{^{207}\mathrm{Pb}—^1\mathrm{H}}$, coupling constant of $\mathrm{PbH_4}$ (in hertz), using different correlated methods: Fermi contact (*FC*); spin dipolar (*SD*); orbital paramagnetic (*OP*); orbital diamagnetic (*OD*); spin–orbit (*SO*) correction

Method	FC	SD	OP	OD	OP-FC-SO[a]	Total
RPA	1806.94	−0.36	−6.22	0.02	−198.60	1601.78
SOPPA	1449.96	–	−5.93	0.02	–	1444.05[b]
SOPPA(CCSD)	1374.20	–	−6.11	0.02	–	1368.11[b]
CAS A	1424.00	0.14	−5.75	0.03	–	1418.42
CAS B	1414.25	–	−5.65	0.02	–	1408.63[b]
CAS C	1331.73	–	–	0.02	–	1331.75[c]
RAS A	1448.65	0.12	−5.84	0.02	–	1442.95
RAS B	1440.05	0.09	−5.71	0.02	–	1434.44
RAS C	1382.84	0.11	−6.10	0.02	–	1376.87
RAS E	1560.69	–	−5.46	0.02	–	1555.25[b]

[a] Only the one-electron part
[b] Without the SD term
[c] Without the SD and OP terms

Table 5. Two-bond, $^2J_{^1\mathrm{H}-^1\mathrm{H}}$, coupling constant of $\mathrm{PbH_4}$ (in hertz), using different correlated methods

Method	FC	SD	OP	OD	OP-FC-SO[a]	Total
RPA	1.95	−0.01	5.00	−7.06	−0.09	−0.21
SOPPA	9.25	–	5.02	−7.07	–	7.16[b]
SOPPA(CCSD)	8.49	–	5.02	−7.06	–	6.44[b]
CAS A	0.24	−0.01	5.00	−7.05	–	−1.82
CAS B	0.65	–	5.00	−7.05	–	−1.40[b]
CAS C	3.05	–	–	−7.05	–	
RAS A	0.29	−0.01	5.00	−7.05	–	−1.77
RAS B	0.66	−0.01	5.00	−7.05	–	−1.41
RAS C	3.06	−0.01	4.99	−7.05	–	0.98
RAS E	3.07	–	5.00	−7.06	–	1.01[b]

[a] Only the one-electron part
[b] Without the SD term

noncontact terms are not affected by inclusion of electron correlation.

4.2 Geometry dependence of the coupling constants

Figures 1–3 show the dependence of the nonrelativistic $^1J_{\mathrm{Pb-H}}$ and $^2J_{\mathrm{H-H}}$ coupling constants on the symmetric stretching of Pb—H bond length, which is the only normal coordinate contributing to first order. The calculations were carried out at the RPA and valence CAS (CAS A) level only, since in the previous study of the other molecules in the $\mathrm{XH_4}$ series [3] the CAS A and SOPPA coupling constant curves turned out to be nearly parallel. Also, as for the other molecules the RPA $^1J_{\mathrm{Pb-H}}$ and $^2J_{\mathrm{H-H}}$ coupling constant curves are steeper and more curved than the CAS A curves, thus leading to an overestimation of the ZPVA correction. In the case of $^1J_{\mathrm{Pb-H}}$ coupling the FC term obviously determines the geometry dependence, because of its size; however, also for the $^2J_{\mathrm{H-H}}$, where the FC, OP, and OD contributions are of the same order of magnitude, the FC term is the most geometry dependent contribution as can be seen from Fig. 3. It is interesting to note that the SD term is almost independent of the bond length, while the OP and OD contributions exhibit an opposite geometry dependence and their sum increases only very slightly with the bond length. Thus, also in the case of $^2J_{\mathrm{H-H}}$ the change in the total coupling constant is determined by the FC term.

5 Summary and conclusions

The calculations reported here show that the general conclusions from the previous studies of the spin–spin coupling constants of $\mathrm{SiH_4}$, $\mathrm{GeH_4}$, and $\mathrm{SnH_4}$ also apply to $\mathrm{PbH_4}$. The FC term is the all-dominating contribution to the Pb—H coupling and, thus, also determines the geometry dependence. Correlation does not change the importance of the individual contributions, although the FC term is reduced by about 20% and the SD term changes its sign. The spin–orbit correction, here approximated by the one-electron part of the FC–OP cross term, is the second most important contribution to the Pb—H coupling in contrast to the other $\mathrm{XH_4}$ molecules. At the RPA level it amounts to 10% of the FC term and is thus, as expected, much larger than for $\mathrm{SnH_4}$. Since scalar relativistic effects can also be expected to be very important for $\mathrm{PbH_4}$, it is not possible from our calculations to estimate the total relativistic correction to the coupling constants as would be inherently included in a four-component relativistic linear-response calculation [14]; however, our results can serve as uncorrelated and correlated nonrelativistic reference values. Comparison of our nonrelativistic results with the results of future uncorrelated and correlated four-

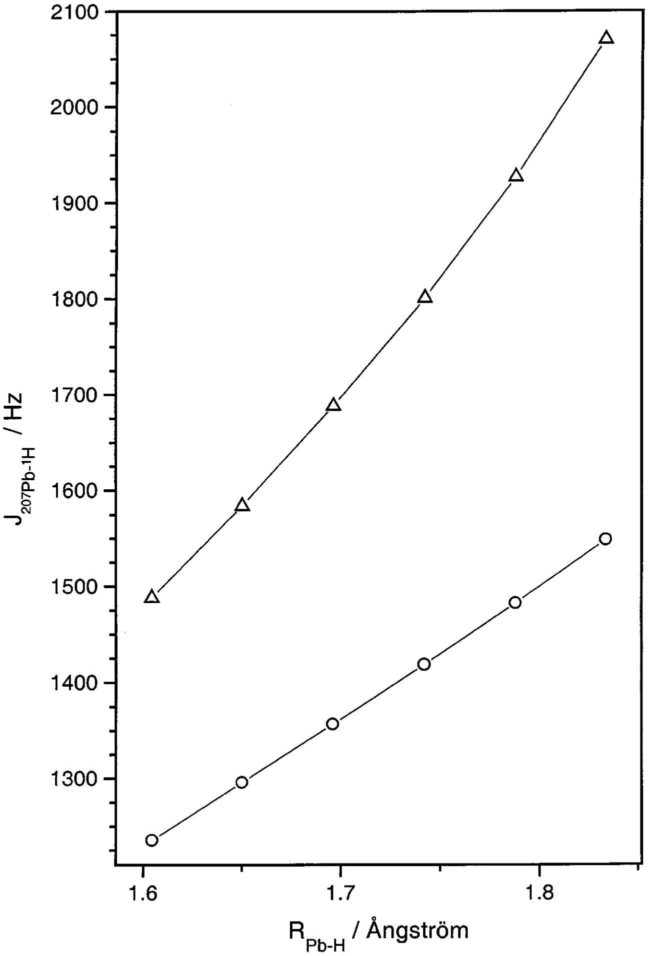

Fig. 1. Total $^1J_{^{207}\mathrm{Pb}-^1\mathrm{H}}$ coupling constant at the random phase approximation (*RPA*) (△) and complete active space (*CAS*) A (○) level

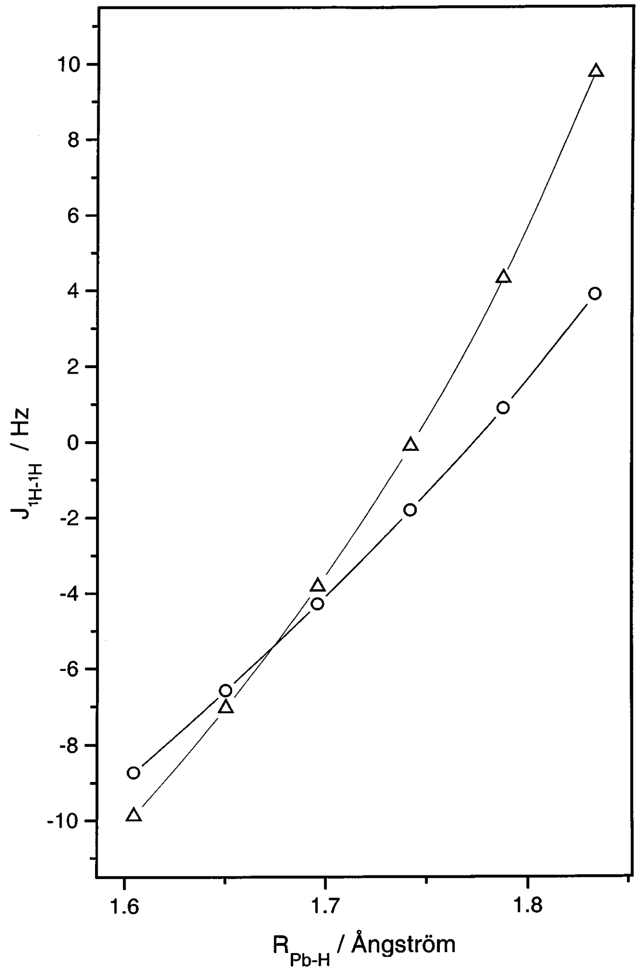

Fig. 2. Total $^2J_{^1H-^1H}$ coupling constant at the RPA (△) and CAS A (○) level

component relativistic calculations will give the total relativistic correction to the coupling constants. Furthermore, comparing this total relativistic correction with the spin–orbit contribution of this work will yield an estimate of the nonscalar relativistic correction, which cannot be obtained directly from four-component relativistic linear-response calculations.

Also for the calculated H—H coupling constants agreement is found with the trends observed in the other molecules of this series. The FC term is thus not the dominating contribution, since the OP and OD contributions are also of equal importance. Correlation affects again only the FC term; however, as also seen for GeH_4 and SnH_4, the different correlation methods do not agree on the sign of the correlation correction.

The geometry dependence of both spin–spin coupling constants is overestimated at the RPA level. The Fermi contact contribution exhibits the largest bond-length dependence and thus determines the form of the coupling constant surfaces.

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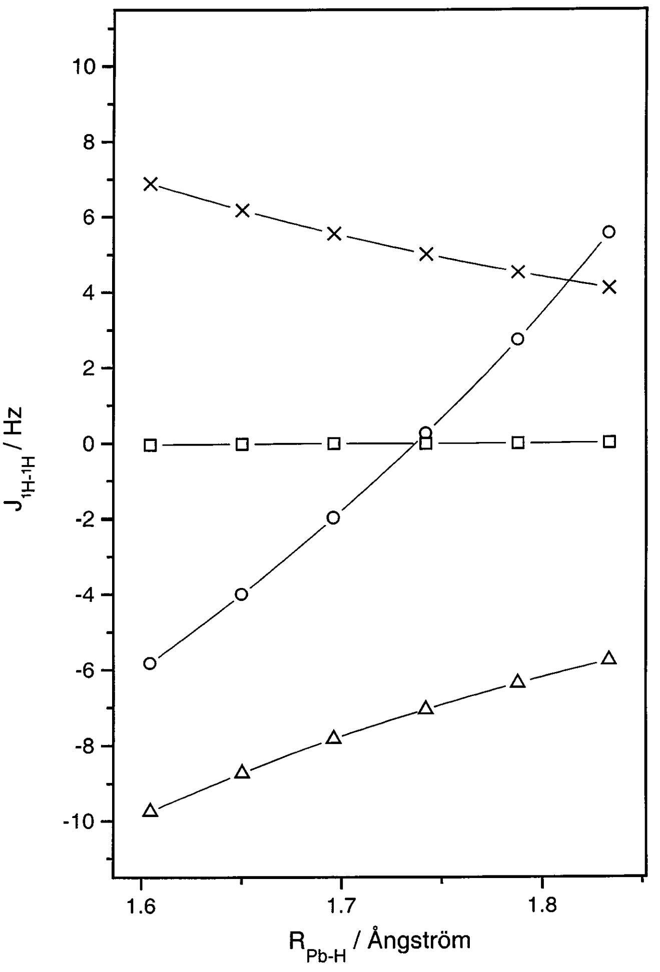

Fig. 3. CAS A calculations of the individual contributions (Fermi contact ○, spin dipolar □, orbital paramagnetic ×, orbital diamagnetic △) to the $^2J_{^1H-^1H}$ coupling constant

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