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Ab initio MO studies of nuclear spin–spin coupling constants in CH_4, SiH_4, AlH_4^- and GeH_4 systems

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Summary. *Ab initio* molecular orbital calculations of electron coupled nuclear spin–spin coupling constants are performed for CH_4, SiH_4, AlH_4^- and GeH_4 systems using the SCF perturbation theory. Basis set dependence of the major contributing terms such as orbital diamagnetic, orbital paramagnetic, spin dipolar and Fermi contact terms are studied. The study also illustrates the relative importance of bond centred functions and nuclear centred polarization functions in predicting the directly bonded and geminal couplings in the systems selected. Basis sets having uncontracted core *s* functions and augmented with bond functions seem to predict most of these couplings fairly satisfactorily when compared to the experimental values.

Key words: *Ab initio* – Spin–spin coupling constants – Bond centred functions

Introduction

Electron coupled nuclear spin–spin coupling constant is one of the important molecular parameters observed in high resolution NMR spectroscopy of fluids and is a measure of the energy of interaction between two magnetic nuclei in different parts of the same molecule. After the first theoretical explanation by Ramsey [1], different theoretical approaches at various levels of approximation as well as at *ab initio* level have been employed by many workers in the past to compute this second order property. Good reviews of these studies are written by Kowalewski [2], Fukui [3] and Oddershede [4]. Ditchfield and Snyder [5] evaluated all the four major contributing terms to nuclear spin couplings in CH_3F by employing the *ab initio* SCF perturbation theory. Kowalewski and coworkers [6–10] performed non empirical calculations of Fermi contact contributions to nuclear spin couplings in a number of systems. Guest et al. [11], Guest and Overill [12] and Overill and Guest [13] carried out extensive calculations of nuclear spin coupling constants for a series of molecules. Also, there exist other methods such as first order polarization propagator approach (FOPPA) by Lazzeretti et al. [14], the equations of motion (EOM) method at *ab initio* level by Fronzoni and Galasso [15, 16] and Galasso [17], second order polarization propagator approach (SOPPA) by Geertsen et al. [18] and the coupled cluster polarization propagator approach

(CCPPA) by Geertsen [19] for the evaluation of indirect nuclear spin–spin Couplings. coupled cluster singles and doubles polarization propagator approach (CCSDPPA) has been employed by Scuseria and coworkers [20, 21] to have a better estimate of correlation contribution to spin–spin couplings, than was available in earlier methods. Fukui et al. [22] have employed many body perturbation theory (MBPT) to calculate the electron correlation contribution to Fermi contact term. All these calculations are restricted to small molecules. Recently Malkin et al. [23] have employed a density functional approach to calculate coupling constants in large molecules with encouraging results.

The present study is concerned with the basis set dependence of the coupling constants at *ab initio* level by employing the SCF perturbation theory put forward by Blizzard and Santry [24]. It also illustrates the relative importance of bond centred functions and polarization functions in predicting different couplings. The basis set dependence of different contributing mechanisms to spin couplings namely, orbital diamagnetic (OD), orbital paramagnetic (OP), spin dipolar (SD), and Fermi contact (FC), has also been examined. The molecular systems studied include CH_4, SiH_4, AlH_4^- and GeH_4.

Theoretical methods

According to Ramsey [1], the nuclear spin dependent terms in the Hamiltonian for the interaction of a molecule with electromagnetic field are as under,

$$\mathscr{H}^{1a} = \frac{1}{2c^2} \sum_k \sum_N \sum_{N'} \gamma_N \gamma_{N'} \left(\frac{I_N \times r_{kN}}{r_{kN}^3} \right) \left(\frac{I_{N'} \times r_{kN'}}{r_{kN'}^3} \right), \tag{1}$$

$$\mathscr{H}^{1b} = \frac{1}{ci} \sum_k \sum_N \gamma_N \frac{I_N L_{kN}}{r_{kN}^3}, \tag{2}$$

$$\mathscr{H}^{2} = \frac{1}{c} \sum_k \sum_N \gamma_N \left[\frac{3(S_k r_{kN})(I_N r_{kN})}{r_{kN}^5} - \frac{S_k I_N}{r_{kN}^3} \right], \tag{3}$$

$$\mathscr{H}^{3} = \frac{8\pi}{3c} \sum_k \sum_N \gamma_N \, \delta(r_{kN}) S_k I_N, \tag{4}$$

$\mathscr{H}^{1a}$ corresponds to the orbital diamagnetic interaction, $\mathscr{H}^{1b}$ corresponds to the orbital paramagnetic interaction, $\mathscr{H}^{2}$ represents the spin dipolar interaction and $\mathscr{H}^{3}$ is the Hamiltonian for the Fermi contact interaction.

Here, γ_N represents the magnetogyric ratio of the nucleus N, I_N the spin angular momentum of nucleus N, L_{kN} the orbital angular momentum of the kth electron about nucleus N, S_k the spin angular momentum of the electron k, r_{kN} is the radius vector from the Nth nucleus to the kth electron and $\delta(r_{kN})$ is the Dirac delta function which picks up values at $r_{kN} = 0$.

The theoretical treatment of these contributing mechanisms at *ab initio* level by employing the SCF perturbation theory [24, 25] is discussed in detail elsewhere [26, 27]. Following these methods, the four major contributions to indirect nuclear spin coupling constant can be given as

$$J^{1a}_{N_\lambda N'_\sigma} = \left(\frac{\hbar}{2\pi}\right)\frac{\gamma_N\gamma_{N'}}{2c^2}\sum_\mu\sum_\nu P_{\mu\nu}\left\langle \mu\left|\frac{[\boldsymbol{r}_{kN}\boldsymbol{r}_{kN'})\delta_{\lambda\sigma} - (\boldsymbol{r}_{kN'})_\lambda(\boldsymbol{r}_{kN})_\sigma]}{\boldsymbol{r}^3_{kN}\,\boldsymbol{r}^3_{kN'}}\right|\nu\right\rangle, \tag{5}$$

$$J^{1b}_{N_\lambda N'_\sigma} = \left(\frac{\hbar}{2\pi c}\right)\gamma_N\gamma_{N'}\sum_\mu\sum_\nu P^{im'}_{\mu\nu}\left\langle \mu\left|\frac{(L_{kN'})_\sigma}{\boldsymbol{r}^3_{kN}}\right|\nu\right\rangle, \tag{6}$$

$$J^2_{N_x N'_x} = \left(\frac{\hbar}{2\pi}\right)\gamma_N\gamma_{N'}\sum_\mu\sum_\nu \Big[(\boldsymbol{P}^{\alpha\beta'}_{\mu\nu} + \boldsymbol{P}^{\beta\alpha'}_{\mu\nu})(\boldsymbol{h}_{xx})_{\mu\nu}$$

$$+ (\boldsymbol{P}^{\alpha'\beta}_{\mu\nu} - \boldsymbol{P}^{\beta\alpha'}_{\mu\nu})(\boldsymbol{h}_{xy})_{\mu\nu} + 2\boldsymbol{P}^{\alpha\alpha'}_{\mu\nu}(\boldsymbol{h}_{xz})_{\mu\nu}\Big], \tag{7}$$

$$J^3_{N_\lambda N'_\lambda} = \left(\frac{\hbar}{2\pi}\right)\gamma_N\gamma_{N'}\sum_\mu\sum_\nu \boldsymbol{P}^{\alpha'}_{\mu\nu}\langle\mu|\boldsymbol{h}^3_{N'}|\nu\rangle, \tag{8}$$

where J^{1a}, J^{1b}, J^2 (equation given here is for the x component only and similarly for y and z components [26]) and J^3 are the OD, OP, SD and FC contributions of nuclear spin–spin coupling constants, respectively.

Computational details

The computer program, based on the work of Chandra and Buenker [28, 29], which was in use for the evaluation of nuclear quadrupole coupling constants [30–34], was modified to compute contributions to coupling constants from different contributing mechanisms.

In the present study, we have attempted to find moderately sized basis sets augmented with nuclear centred (PF) and/or bond centred (BF) polarization functions, which could give reasonably good predictions of the nuclear spin couplings in the molecular systems selected. Since the Fermi contact term is the dominant contributor to couplings involving protons, the effect of uncontracting core *s* functions has also been examined.

Results and discussion

In this section, we discuss the C–H, Si–H, Al–H, Ge–H and H–H couplings in systems CH_4, SiH_4, AlH_4^- and GeH_4. The couplings calculated involve nuclei, ^{13}C, ^{19}Si, ^{27}Al, ^{73}Ge and ^1H. The basis sets employed in the calculation are as follows: For carbon, a (9*s* 5*p*) basis set [35], first contracted to [4*s* 2*p*] with a contraction pattern, (6, 1, 1, 1 ; 4, 1) and then to [5*s* 2*p*] by uncontracting the innermost *s* function, viz, (1, 5, 1, 1, 1 ; 4, 1) and finally a [9*s* 2*p*] basis set is obtained by uncontracting all the *s* functions, with a contraction pattern, (1, 1, 1, 1, 1, 1, 1, 1, 1 ; 4, 1). For silicon and aluminium, a (12*s* 7*p*) basis [36] was first contracted to [6*s* 4*p*] as (6, 3, 1, 1, 1, 1 ; 5, 2, 1, 1) and later a [12*s* 4*p*] basis was employed by uncontracting all the *s* functions giving a pattern (1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1 ; 5, 2, 1, 1). For germanium, a (13*s* 9*p* 5*d*) basis set [37] contracted to [13*s* 6*p* 2*d*] following a pattern, (1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1 ; 4, 1, 1, 1, 1, 1 ; 4, 1) is employed. For the hydrogen atom, a (4*s*) basis set [35] contracted to [2*s*] in the pattern (3, 1) is used. Other variations of this basis set included uncontracted patterns (1, 2, 1) and

(1, 1, 1, 1). Besides these, use is also made of a nearly triple zeta quality basis set, viz, (10*s* 6*p*) [38] contracted to [5*s* 3*p*] and (5*s*) [38] contracted to [3*s*] for carbon and hydrogen, respectively. The scale factor used for hydrogen atom exponents is 1.2 for the different contraction patterns of the (4*s*) basis set and 1.44 for the (5*s*) basis set.

All these basis sets are augmented with nuclear centred polarization functions (PFs), exponents of which are taken from literature [39] as well as bond centred polarization functions (BFs), exponents of which are obtained by optimizing them with respect to energy using a double zeta (DZ) quality basis set.

Buenker and coworkers [40–42] have used bond functions in theoretical calculations of dissociation energies in several molecules. Chandra and coworkers [30–34], used these functions for the evaluation of nuclear quadrupole coupling constants in a large number of systems. Their calculations suggest that the use of bond functions in basis sets generally gives results which are at least as accurate as those obtained with polarization functions in the basis set, and yet it is more economical.

(i) CH_4

Nuclear spin–spin couplings in methane have been calculated by a number of workers employing different theoretical techniques [11, 12, 17, 21–23, 43, 44]. In the present work, we have studied the basis set dependence of four contributors to C–H and H–H nuclear spin couplings in methane at its experimental geometry [45]. The computed results with various basis sets are tabulated in Table 1 along with other theoretical [12, 22] and experimental [46, 47] results.

On employing a [4*s* 2*p*/2*s*] basis set, the calculated $^1J_{CH}$ coupling is found to be much larger than the experimental value. When bond centred functions are added to this basis set, the $^1J_{CH}$ value is reduced by about 29.56 Hz and is comparable to the experimental value. Augmentation of the DZ quality basis set with PFs resulted in a $^1J_{CH}$ coupling of 147.44 Hz which is only 18.71 Hz lower than that due to the DZ basis. When both BFs and PFs are added to the DZ quality basis set, the corresponding lowering in calculated coupling is almost the same (18.06 Hz). Out of these four basis sets employed, the coupling obtained with DZ quality basis set augmented with BFs (136.59 Hz) is found closest to the experimental coupling (120.8 ± 0.05 Hz).

The [5*s* 3*p*/3*s*] basis set (obtained by contracting the (10*s* 6*p*/5*s*) basis) by itself or with bond functions and/or polarization functions yielded $^1J_{CH}$ values, which are much higher than those calculated with their double zeta counterparts, as well as higher than the experimental value.

When the contraction pattern of the inner *s* functions in the [4*s* 2*p*/2*s*] basis set is changed to a more relaxed inner core by just uncontracting the innermost *s* functions of carbon and hydrogen bases, the resulting [5*s* 2*p*/3*s*] basis set yielded a $^1J_{CH}$ value of 148.35 Hz which is 17.80 Hz lower than that due to the DZ quality basis set. It is also interesting to note that this result is close to that obtained with [4*s* 2*p*/2*s*] + PF basis set. When this uncontracted basis set is augmented with PFs, the obtained $^1J_{CH}$ coupling (134.83 Hz) is about 12.61 Hz lower than that due to the [4*s* 2*p*/4*s*] + PF basis set. This result is comparable to the experimental value.

This observed improvement in $^1J_{CH}$ coupling value due to the uncontraction of the innermost *s* function each of the carbon and hydrogen basis sets prompted us to

Table 1. Basis set, energy and nuclear spin coupling constants in CH_4

Basis set[a]	Energy (a.u.)	Coupling	Spin–spin coupling constants (Hz)				
			OD	OP	SD	FC	Total
[4*s* 2*p*/2*s*]	−40.18537	C–H	0.19	0.19	0.04	165.73	166.15
		H–H	−1.59	0.41	0.94	−31.87	−32.11
[4*s* 2*p*/2*s*] + BF	−40.20286	C–H	0.13	0.04	0.36	136.06	136.59
		H–H	−1.71	0.82	0.91	−27.12	−27.10
[4*s* 2*p*/2*s*] + PF	−40.20600	C–H	0.13	0.13	−0.35	147.53	147.44
		H–H	−1.72	0.72	0.74	−26.15	−26.41
[4*s* 2*p*/2*s*] + BF + PF	−40.20762	C–H	0.13	0.19	−0.03	147.80	148.09
		H–H	−1.72	0.91	1.01	−24.80	−24.60
[5*s* 3*p*/3*s*]	−40.18992	C–H	0.19	0.46	−0.75	157.99	157.89
		H–H	−1.60	0.07	1.06	−27.57	−28.04
[5*s* 3*p*/3*s*] + BF	−40.20940	C–H	0.12	0.14	0.94	153.39	154.59
		H–H	−1.73	1.48	3.00	−26.60	−23.85
[5*s* 3*p*/3*s*] + BF + PF	−40.21230	C–H	0.13	0.22	0.22	150.60	151.17
		H–H	−1.73	1.54	3.06	−26.95	−24.08
[5*s* 2*p*/3*s*]	−40.18543	C–H	0.19	0.19	0.05	147.92	148.35
		H–H	−1.59	0.27	0.92	−24.76	−25.15
[5*s* 2*p*/3*s*] + PF	−40.20712	C–H	0.13	0.12	−0.21	134.79	134.83
		H–H	−1.71	0.72	0.74	−21.35	−21.60
[9*s* 2*p*/4*s*]	−40.18691	C–H	0.19	0.19	0.13	136.39	136.90
		H–H	−1.59	0.28	0.90	−23.73	−24.14
[9*s* 2*p*/4*s*] + BF	−40.20475	C–H	0.13	0.04	0.36	131.88	132.41
		H–H	−1.72	0.82	0.87	−22.65	−22.68
[9*s* 2*p*/4*s*] + PF	−40.20775	C–H	0.13	0.15	−0.47	130.69	130.50
		H–H	−1.72	0.74	0.76	−21.15	−21.37
[9*s* 2*p*/4*s*] + BF + PF	−40.20842	C–H	0.13	0.20	−0.23	130.95	131.05
		H–H	−1.72	0.91	0.91	−21.60	−21.50
Other theoretical values (i)[b]		C–H					113.0
		H–H					−14.0
(ii)[c]		C–H					129
		H–H					−20.5
Experimental values[d]		C–H					120.78
		H–H					−12.56

[a] Optimized BF exponents for C–H bond are: $\alpha_s = 1.0$ and $\alpha_p = 0.6$

[b] Ref. [11]

[c] Ref. [22]

[d] Ref. [46, 47]

completely uncontract the core *s* functions of these basis sets. The results obtained with such basis sets are found to be in gratifying agreement with experiment.

As already mentioned above, in going from DZ to [5*s* 2*p*/3*s*], $^1J_{CH}$ value was lowered by 17.80 Hz; on further uncontraction, the [9*s* 2*p*/4*s*] basis resulted in further lowering of this coupling by 11.45 Hz. Comparing the $^1J_{CH}$ value due to [9*s* 2*p*/4*s*] + BF basis with its contracted counterpart, the [4*s* 2*p*/2*s*] + BF basis set, the former yielded a coupling value of 132.41 Hz which is only 4.18 Hz lower than that due to the latter. A similar comparison of the results due to [9*s* 2*p*/4*s*] + PF and [4*s* 2*p*/2*s*] + PF basis sets reveals that $^1J_{CH}$ coupling obtained with the former basis set is about 16.94 Hz lower than that obtained with the latter. The largest basis set that we employed for this molecule, namely the [9*s* 2*p*/4*s*] + BF + PF basis, yielded a coupling value of 131.05 Hz which is 17.04 Hz lower in magnitude than that due to the [4*s* 2*p*/2*s*] + BF + PF basis set. A close scrutiny of these results reveals that the calculated $^1J_{CH}$ is much more stable to uncontraction of core *s* functions, when DZ + BF basis set is employed compared to the cases where DZ, DZ + PF or DZ + BF + PF basis sets are employed.

Regarding the relative significance of different contributing terms, except FC term all other terms are found to be negligibly small. The agreement which we obtained between the results due to [9*s* 2*p*/4*s*] + BF (132.41 Hz), [9*s* 2*p*/4*s*] + PF (130.50 Hz) and [9*s* 2*p*/4*s*] + BF + PF (131.05 Hz) basis sets with the experimental value is fairly satisfactory. Geertsen et al. [21] have employed various polarization propagator approaches to study the basis set dependence of $^1J_{CH}$ and $^2J_{HH}$ in methane employing very large basis sets and have got $^1J_{CH}$ values in the range, 115–130 Hz. They have demonstrated that the correlation effects are very important. Fukui et al. [22] have also studied these couplings in CH_4 and have shown that Fermi contact contribution to $^1J_{CH}$ is 167 (156), 147 (136), 143 (131) and 141 (129) Hz for 6–31G, 6–31G* and 6–31G** basis sets, respectively. The numbers in parenthesis refer to coupling values obtained after the correlation corrections have been incorporated. Employing these results it is estimated that our uncorrelated Fermi contact term of 130.95 Hz for the largest basis set employed by us should correspond to a correlated Fermi contact term of around 118.5 Hz and thus corresponds to a total $^1J_{CH}$ of about 120 Hz in excellent agreement with experimental value of 120.8 Hz.

The geminal H–H coupling ($^2J_{HH}$) in this molecule is found to be overestimated by most of the basis sets which we employed, nevertheless a good trend is observed on increasing the number of functions in the basis set. The effect of uncontraction of the innermost *s* function of the DZ basis set to this coupling is about 6.96 Hz, the corresponding difference to its PF counterpart is 4.81 Hz. Uncontraction of all core *s* functions of the [4*s* 2*p*/2*s*] basis resulted a change of 7.97 Hz to the $^2J_{HH}$ coupling value (which is $-$ 24.14 Hz and is only 1.01 Hz lower in magnitude than that due to the [5*s* 2*p*/3*s*] basis). [9*s* 2*p*/4*s*] + BF basis set yielded $^2J_{HH}$ value of about $-$ 22.68 Hz which is only 3.73 Hz lower in magnitude than that due to its contracted counterpart. The corresponding difference in this coupling obtained for the basis sets augmented with PFs is found to be 5.04 Hz. Uncontraction of the core *s* functions of [4*s* 2*p*/2*s*] + BF + PF basis resulted in a change in magnitude of this geminal coupling by about 3.10 Hz, which is comparable to that observed for the basis set augmented with only BFs. The reported higher value of this coupling may be due to a large electron correlation contribution to the Fermi contact term. Overill and Guest [13] reported an electron correlation correction of about 46.5% of their otherwise evaluated FC term for this coupling. The correlation effects calculated for $^2J_{HH}$ by Fukui et al. [22] as well as Geertsen et al. [21] bring the calculated coupling closer to the experimental value, but still the agreement is not very good.

(ii) SiH_4

Theoretical studies of spin couplings in SiH_4 were carried out by employing the first order polarization propagator approach (FOPPA) by Lazzeretti et al. [14] and by using *ab initio* SCF perturbation calculations by Overill and Guest [13]. In our study, the calculated $^1J_{SiH}$ and $^2J_{HH}$ couplings in this molecule are for its experimental geometry [48]. The calculated coupling constants along with energy optimized exponents of bond functions are reported in Table 2. Among the DZ series of basis sets with BFs and PFs, the [6*s* 4*p*/2*s*] + BF + PF basis set predicts $^1J_{SiH}$ coupling constant which is closest to experiment. The result of basis set with BFs approaches the result of basis set with both BFs and PFs faster than that of the basis set with PFs alone. Uncontraction of the core *s* functions resulted in a reduction in magnitude of 26.11, 25.05, 30.07 and 22.06 Hz for [12*s* 4*p*/4*s*], [12*s* 4*p*/4*s*] + BF, [12*s* 4*p*/4*s*] + PF and [12*s* 4*p*/4*s*] + BF + PF basis sets, respectively. The best result is obtained with the [12*s* 4*p*/4*s*] + BF + PF basis set, which

Table 2. Basis set, energy and nuclear spin coupling constants in SiH_4

Basis set[a]	Energy (a.u.)	Coupling	Spin–spin coupling constants (Hz)				
			OD	OP	SD	FC	Total
[6*s* 4*p*/2*s*]	– 291.19746	Si–H	– 0.05	– 0.12	1.28	– 271.90	– 270.79
		H–H	– 1.08	0.10	0.14	– 12.79	– 13.63
[6*s* 4*p*/2*s*] + BF	– 291.25187	Si–H	– 0.01	0.16	1.51	– 236.64	– 234.98
		H–H	– 1.18	0.14	0.15	– 1.49	– 2.38
[6*s* 4*p*/2*s*] + PF	– 291.23878	Si–H	– 0.01	0.01	– 4.55	– 240.44	– 244.99
		H–H	– 1.18	0.21	0.18	– 4.62	– 5.41
[6*s* 4*p*/2*s*] + BF + PF	– 291.25423	Si–H	– 0.01	0.12	0.78	– 231.44	– 230.55
		H–H	– 1.18	0.24	0.15	– 0.76	– 1.55
[12*s* 4*p*/4*s*]	– 291.19797	Si–H	– 0.05	0.03	0.48	– 245.15	– 244.68
		H–H	– 1.09	0.10	0.06	– 10.65	– 11.58
[12*s* 4*p*/4*s*] + BF	– 291.24930	Si–H	– 0.01	0.05	1.15	– 211.12	– 209.93
		H–H	– 1.18	0.13	0.16	– 1.70	– 2.59
[12*s* 4*p*/4*s*] + PF	– 291.24100	Si–H	– 0.01	0.06	0.26	– 215.23	– 214.92
		H–H	– 1.18	0.21	0.17	– 2.45	– 3.25
[12*s* 4*p*/4*s*] + BF + PF	– 291.25138	Si–H	– 0.01	0.02	0.70	– 209.20	– 208.49
		H–H	– 1.18	0.23	0.13	– 1.27	– 2.09
Other theoretical values	(i)[b]	Si–H					– 178.7
		H–H					– 0.4
	(ii)[c]	Si–H					– 236.3
		H–H					– 2.26
Experimental values[d]		Si–H					– 202.5
		H–H					– 2.75

[a] Optimized BF exponents for Si–H bond are: $\alpha_s = 0.5$, $\alpha_p = 0.1$

[b] Ref. [13]

[c] Ref. [14]

[d] Ref. [49]

gives a coupling value of − 208.49 Hz, only about 6 Hz higher in magnitude than the experimental coupling (− 202.5 Hz) [49]. Overill and Guest [13] have performed an electron correlation correction and their final $^1J_{\mathrm{SiH}}$ value thus obtained is − 178.7 Hz. The contributions from the noncontact terms to this coupling are found to be negligibly small.

As far as the geminal H–H coupling in this molecule is concerned, the results compare well with experiments only if bond functions are present in the basis set, with (− 1.55 Hz) or without (− 2.38) polarization functions. The result with DZ and DZ + PF basis sets are too far from experiment. The uncontraction of core *s* functions of the basis set from [6*s* 4*p*/2*s*] to [12*s* 4*p*/4*s*] does not alter this trend. Here again, the coupling calculated with [12*s* 4*p*/4*s*] basis set is far from the experimental value. The effect of uncontraction on DZ + PF basis makes a significant improvement in the result and the final coupling is close to experiment. On the other hand, couplings obtained with [12*s* 4*p*/4*s*] + BF and [12*s* 4*p*/4*s*] + BF + PF basis sets are − 2.59 and − 2.09 Hz are in reasonably good agreement with experiment and are only minor improvement over their contracted counterparts. Another noteworthy feature of this coupling is that the contribution of orbital diamagnetic (OD) term (which is − 1.18 Hz) for both [12*s* 4*p*/4*s*] + BF and [12*s* 4*p*/4*s*] + BF + PF basis sets is comparable to the Fermi contact contributions of − 1.70 and − 1.27 Hz, respectively from these basis sets. This implies that for a fairly good prediction of $^2J_{\mathrm{HH}}$ coupling in $\mathrm{SiH_4}$, the OD term cannot be neglected. Our study of many molecules have revealed that the orbital diamagnetic term, which depends on the knowledge of density matrix, is not a very sensitive function of the basis set. On the other hand, other terms depend on the derivatives of density matrix and are sensitive to the size of the basis set, unless the latter is very large. In present case of geminal coupling in $\mathrm{SiH_4}$, whereas the orbital term is almost independent of the size of the basis set, the Fermi contact term is strongly dependent on the basis set and these two terms are comparable in magnitude, thereby rendering the total coupling not very sensitive to the size of the basis set. Such is not the case in $\mathrm{CH_4}$, where OD term is negligible compared to FC term and hence the total coupling is a sensitive function of the basis set.

(iii) $\mathrm{AlH_4^-}$

Results obtained for $\mathrm{AlH_4^-}$ are listed in Table 3. To the best of our knowledge, there exists only one theoretical calculation of spin couplings for this ion, which is by employing the first order polarization propagator approach [14]. The geometry employed in the present study is the SCF optimized geometry [50] obtained by employing a STO-3G* basis set. The bond centred functions (BFs) employed are both *s* and *p* types and their optimized exponents are also given in Table 3.

Like other X–H couplings (X being the heavy atom) discussed earlier, here also the FC term makes the dominant contribution to $^1J_{\mathrm{AlH}}$ coupling while all other contributions fall well below 0.1 Hz in magnitude for most of the basis sets used. The use of DZ basis set is not tested in this molecule as it is found inadequate in predicting the couplings in other systems. A good agreement of our computed results exists with the reported FOPPA results [14]. Results obtained with the [12*s* 4*p*/4*s*] + BF (134.61 Hz) and [12*s* 4*p*/4*s*] + BF + PF (133.88 Hz) are found to be closer to the experimental $^1J_{\mathrm{AlH}}$ coupling (110.0 Hz [51], than the result for [12*s* 4*p*/2*s*] + PF basis set (155.50 Hz). Regarding the effect of uncontraction of basis sets, uncontraction of core *s* functions of [6*s* 4*p*/2*s*] + BF basis set to

Table 3. Basis set, energy and nuclear spin coupling constants in AlH_4^- ion.

Basis set[a]	Energy (a.u.)	Coupling	Spin–spin coupling constants (Hz)				
			OD	OP	SD	FC	Total
[6s 4p/2s] + BF	− 244.21129	Al–H	0.05	− 0.14	− 0.84	147.87	146.94
		H–H	− 0.90	0.33	− 0.01	− 4.55	− 5.13
[6s 4p/2s] + PF	− 244.19068	Al–H	0.05	− 0.11	− 0.03	155.59	155.50
		H–H	− 0.94	0.21	0.08	− 8.77	− 9.42
[6s 4p/2s] + BF + PF	− 244.21380	Al–H	0.05	− 0.15	− 0.37	141.86	141.39
		H–H	− 0.91	0.53	0.06	− 4.18	− 4.50
[12s 4p/4s]	− 244.18673	Al–H	0.08	− 0.09	− 0.17	157.24	157.06
		H–H	− 0.84	0.12	0.02	− 8.63	− 9.33
[12s 4p/4s] + BF	− 244.21859	Al–H	0.06	− 0.15	0.55	134.15	134.61
		H–H	− 0.90	0.17	0.09	− 4.35	− 4.99
[12s 4p/4s] + PF	− 244.21111	Al–H	0.05	− 0.12	− 0.02	139.15	139.06
		H–H	− 0.91	0.18	0.08	− 5.26	− 5.91
[12s 4p/4s] + BF + PF	− 244.21995	Al–H	0.05	− 0.14	0.49	133.48	133.88
		H–H	− 0.91	0.21	0.11	− 4.54	− 5.13
Other theoretical values[b]		Al–H					+ 146.
		H–H					− 6.
Experimental values[c]		Al–H					110.
		H–H					—

[a] Optimized BF exponents for Al–H bond are: $\alpha_s = 0.3$, $\alpha_p = 0.25$

[b] Ref. [14]

[c] Ref. [51]

[12s 4p/4s] + BF resulted in a betterment of the Al–H coupling by about 12.33 Hz. The relaxation of core s functions of [6s 4p/4s] + PF basis set yielded a change in Al–H coupling by 16.44 Hz where as the corresponding change in moving from [6s 4p/2s] + BF + PF basis to [12s 4p/4s] + BF + PF basis set is only 7.51 Hz, and is fairly close (133.38 Hz) to the experimental value (110.0 Hz).

No experimental ${}^2J_{\mathrm{HH}}$ coupling is reported for this molecule. For this coupling, the major contributing interaction is the FC interaction, the next major contribution is from the OD term which is, for the [12s 4p/4s] + BF + PF basis set, about 17.7% of the total coupling value. The computed values for basis sets containing BFs, PFs or both are comparable to the previously reported theoretical value [14]. As seen earlier in the case of SiH_4 molecule, the result of DZ + BF basis set is comparable to that of DZ + BF + PF basis set. On the other hand, the result of DZ + BF basis set is very different. The uncontraction of core s functions results in [12s 4p/4s] basis set which gives comparable ${}^1J_{\mathrm{AlH}}$ couplings, whether it is augmented by BFs, PFs and BF + PFs. Thus uncontraction of core seems to effect the core + PF basis set more than core + BF basis set.

However, the geminal H–H coupling in this system follow CH_4 more closely than SiH_4, for the simple reason that in SiH_4, the OD and FC terms are comparable (and hence the total coupling is not very sensitive to change of basis set). On the other hand, in AlH_4^-, OD term is much smaller (about 15–20%) than

FC contribution. Hence in AlH_4^-, where experimental results are not available for this coupling, the calculated values should resemble CH_4 more than SiH_4.

(iv) GeH_4

GeH_4 having a heavy atom has been subjected to very few theoretical calculations and to the best of our knowledge, so far no *ab initio* calculations of nuclear spin couplings for this molecule are reported. However, there exists a relativistically parameterized extended Hûckel calculation of reduced coupling constants by Pyykkö and Wiesenfield [52]. In the present study, following the results obtained for the previously discussed smaller systems, we have used the basis sets which have all the core *s* functions uncontracted, augmented with BFs or PFs to calculate the ${}^1J_{GeH}$ and ${}^2J_{HH}$ couplings. The geometry employed for this calculation is the experimental one [45]. The computed results and the exponents of bond functions are reported in Table 4. Due to the relatively large size of the system, we could use only three basis sets, viz, [13*s* 6*p* 2*d*/4*s*], [13*s* 6*p* 2*d*/4*s*] + BF and [13*s* 6*p* 2*d*/4*s*] + PF in the calculation.

In the ${}^1J_{GeH}$ coupling, as in other cases, the most dominant part is the FC term and all other terms are negligibly small. The results obtained with all the basis sets namely, [13*s* 6*p* 2*d*/4*s*], [13*s* 6*p* 2*d*/4*s*] + BF and [13*s* 6*p* 2*d*/4*s*] + PF are found to be close to the experimental value [53]. For a better understanding of the relative importance of BFs and PFs it would be necessary to use a [13*s* 6*p* 2*d*/4*s*] + BF + PF basis set, but it could not be attempted. It is to be noted that the fairly good agreement obtained for this coupling with experiment (see Table 4) is without any electron correlation correction or any relativistic correction.

The ${}^2J_{HH}$ values obtained for this molecule with all the three basis sets we used are not satisfactory when compared with the experimental value. Only noteworthy

Table 4. Basis set, energy and nuclear spin coupling constants in GeH_4

Basis set[a]	Energy (a.u.)	Coupling	Spin–spin coupling constants (Hz)				
			OD	OP	SD	FC	Total
[13*s* 6*p* 2*d*/4*s*]	– 2077.50320	Ge–H	– 0.01	0.01	0.48	– 100.58	– 100.10
		H–H	– 2.27	0.38	0.07	– 1.99	– 3.81
[13*s* 6*p* 2*d*/4*s*] + BF	– 2077.54141	Ge–H	– 0.00	0.05	0.12	– 96.00	– 95.83
		H–H	– 2.34	0.46	0.15	0.86	– 0.87
[13*s* 6*p* 2*d*/4*s*] + PF	– 2077.53729	Ge–H	– 0.00	0.04	0.43	– 95.33	– 94.86
		H–H	– 2.36	0.49	0.14	1.07	0.66
Other theoretical values[b]		Ge–H					– 59.8
		H–H					
Experimental values[c]		Ge–H					– 97.5
		H–H					12.4

[a] Optimized BF exponents for Ge–H bonds are: $\alpha_s = 0.3$, $\alpha_p = 0.25$

[b] Ref. [52]

[c] Ref. [53, 54]

feature of this coupling is that the dominant contribution seems to come from orbital part (OD + OP) which has a constant value of about − 1.9 Hz.

Conclusions

Basis set dependence study of directly bonded and geminal couplings in CH_4, SiH_4, AlH_4^- and GeH_4 molecules reveals that most of the directly bonded couplings in these systems can be evaluated within a limit of 10–20% with a basis set having uncontracted *s* functions and augmented with BFs and/or PFs. Such basis sets give good results even for the geminal H–H couplings in SiH_4 and AlH_4^-. CH_4 is a well known case in which correlation effects play a very significant role. In GeH_4, even relativistic effects might be important, but we did not study them. The directly bonded couplings show marked improvement when the contracted *s* functions of the core basis are uncontracted. However, the basis set which already has BFs is found to be less sensitive to the uncontraction of core *s* functions compared to basis sets which do not have bond functions. The best results are obtained with basis sets having uncontracted core *s* functions along with BFs and PFs. The results obtained with basis sets having uncontracted core *s* functions along with BFs are much closer to best results than the ones obtained with basis set of uncontracted *s* functions and PFs. This clearly establishes that for most of the calculations in which at least one coupling nucleus is a proton, one need not go to very large basis sets, and a basis set with uncontracted core *s* functions and BFs might suffice. This offers a definite computational advantage over the use of polarization functions as the basis set size in former case is much smaller than in the latter. Since Fukui's [22] work demonstrates that the uncorrelated and correlated coupling constants are almost proportional to each other, the BF or BF + PF basis set might yield correlated coupling constants in good agreement with experiment.

Uncontraction of the core *p* functions of the basis sets may have improved the OP and SD terms as these terms depend on functions with nonzero angular momentum quantum numbers. However, this was not attempted as in systems which we have selected, the OP and SD terms are so small that it did not seem worthwhile to increase the size of the basis set to get a few percent change in these terms.

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