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Relativistic four-component calculations of indirect nuclear spin–spin couplings in MH_4 ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) and $\text{Pb}(\text{CH}_3)_3\text{H}$

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Relativistic four-component random phase approximation (RPA) calculations of indirect nuclear spin–spin coupling constants in MH_4 ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) and $\text{Pb}(\text{CH}_3)_3\text{H}$ are presented. The need for tight s -functions also in relativistic four-component calculations is verified and explained, and the effect of omission of (SS–LL) and (SS–SS) two-electron integrals is investigated. Already in GeH_4 we see a relativistic increase in the coupling constant by 12%, and for PbH_4 the effect is a 156% increase for the one-bond coupling. Large relativistic effects are also computed for the two-bonds couplings. We find that the relativistic effects on the one-bond couplings are mainly due to scalar relativistic factors rather than spin–orbit corrections. © 2000 American Institute of Physics. [S0021-9606(00)30408-1]

I. INTRODUCTION

Since Ramsey in 1953 presented his theory of indirect nuclear spin–spin couplings¹ there has been a great effort to make theoretical predictions agree with observed couplings. Ramsey's theory is based on the nonrelativistic Schrödinger equation and the effect of relativity is not explicitly taken care of. For a long time it has been known that relativistic effects in heavy atoms cannot be ignored. Also for nuclear spin–spin couplings this was recognized several years ago. Feney *et al.*² noted that relativistic corrections should be included in order to get precise estimates of the contact energy term. Dalling and Gutowsky³ studied the Z -dependence of the coupling constant and included a relativistic correction in their calculations of one-bond coupling in the group IV tetrahydrides. In their method the s -electron density at the nuclei is multiplied by a relativistic correction factor. Later Pyykkö and Jokisaari⁴ also included a hydrogen-like relativistic correction in a model study of the MH_4 ($\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) molecules. Calculations based on the relativistically parametrized extended Hückel model appeared in 1981 for the same molecules.⁵ In 1994 Kirpekar *et al.*⁶ presented correlated *ab initio* calculations of spin–spin couplings for the MH_4 series for $\text{M}=\text{C}, \text{Si}, \text{Ge}$, and Sn . No relativistic effects were included, but the authors later published spin–orbit corrections to the couplings⁷ for the same four molecules. Also the effect of nuclear motion has been studied⁸ for these molecules. Recently, a nonrelativistic correlated *ab initio* study of PbH_4 with the most important spin–orbit corrections was published.⁹ So far no fully relativistic calculations have been presented for the MH_4 series.

In this article we use the four-component relativistic RPA method based on the Dirac–Coulomb Hamiltonian to calculate spin–spin couplings in the MH_4 molecules. We investigate some integral approximations and test the effect of

tight s -functions. Furthermore we calculate the Pb–H one-bond coupling in $\text{Pb}(\text{CH}_3)_3\text{H}$ in order to be able to compare with available experimental values.¹⁰

II. METHOD

In relativistic theory the interaction between an electron and a magnetic field generated from the vector potential, $\mathbf{A}(\mathbf{r})$, is described by the interaction Hamiltonian

$$H_I = ec \boldsymbol{\alpha} \cdot \mathbf{A}(\mathbf{r}), \quad (1)$$

where $\boldsymbol{\alpha}$ represents the usual 4×4 matrices in standard representation

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix}. \quad (2)$$

For nuclear spin–spin couplings the vector potential describes the fields from magnetic point dipoles centered at the nuclei with a magnetic moment

$$\mathbf{A}(\mathbf{r}) = \frac{\mu_0}{4\pi} \sum_K \gamma_K \frac{\mathbf{I}_K \times \mathbf{r}_K}{r_K^3}, \quad (3)$$

where $\mathbf{r}_K = (\mathbf{r} - \mathbf{R}_K)$, $\mathbf{R}_K$ is the position of nucleus K , $\mathbf{I}_K$ is the nuclear spin, and γ_K is the magnetogyric ratio. The indirect spin–spin coupling constant which represents the isotropic part of the electron mediated interaction between two nuclear spins can be obtained from the zero-energy limit of a linear response function^{11,12} which in the relativistic case takes the form¹³

$$J(K, L) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \right)^2 (ec\hbar)^2 \frac{\gamma_K \gamma_L}{h} \times \sum_i \left\langle \left\langle \frac{(\mathbf{r}_K \times \boldsymbol{\alpha})_i}{r_K^3}; \frac{(\mathbf{r}_L \times \boldsymbol{\alpha})_i}{r_L^3} \right\rangle \right\rangle_{E=0}, \quad (4)$$

where the sum over i runs over the three principal axes. To get the total coupling from Eq. (4) it is necessary to explic-

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TABLE I. Description of the large component basis sets. The exponential parameter, ξ , is extracted from $\xi = \alpha_l \beta^k$, $k=0,1,2,\dots$.

Atom	Basis set	β	α_s	α_p	α_d	α_f	α_g
H	10s3p	3.062 819	0.103 04 ^a	0.315 60			
C	19s10p4d	2.230 517	0.069 24 ^b	0.069 24	0.069 24 ^c		
Si	23s13p5d	2.054 070	0.082 16 ^b	0.082 16	0.082 16 ^c		
Ge	27s16p11d3f	2.042 484	0.081 55 ^b	0.081 55	0.034 02	0.166 57 ^c	
Sn	30s19p14d3f	2.028 595	0.058 40 ^b	0.058 40	0.118 47	0.118 47 ^c	
Pb	35s23p15d12f3g	1.994 481	0.060 75 ^d	0.121 16	0.481 97	0.481 97	0.481 97 ^c

^aFor the three tightest *s*-functions the ratio is β^2 .^bFor the three tightest *s*-functions the ratio is β^3 .^cFor these functions the ratio is β^2 .^dFor the tightest *s*-function the ratio is β^3 .

itly include both the electron–electron and the electron–positron rotations in the response function.^{14,15} However, including electron–positron rotations puts further demands on the basis sets¹⁵ and instead we use the Sternheim approximation,¹⁶ which has proven sufficiently accurate for our present purposes as shown in a series of test calculations.¹⁵ Thus we include only the electron–electron rotations in Eq. (4), which give the paramagnetic contribution. The electron–positron rotations give the diamagnetic contribution, and in the Sternheim approximation this is calculated as an expectation value of the diagonal four-component orbital diamagnetic (OD) operator,

$$J^{\text{OD}}(K,L) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{e^2 \hbar^2}{m_e} \frac{\gamma_K \gamma_L}{h} \langle 0 | \frac{\mathbf{r}_K \cdot \mathbf{r}_L}{r_K^3 r_L^3} | 0 \rangle, \quad (5)$$

where $|0\rangle$ is the four-component relativistic ground state.

In Ramsey's nonrelativistic theory there are four contributions to the coupling constant.¹ Besides the orbital diamagnetic contribution similar to Eq. (5) there are three paramagnetic terms, namely, the singlet orbital paramagnetic (OP) contribution

$$J^{\text{OP}}(K,L) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{m_e} \right)^2 \frac{\gamma_K \gamma_L}{h} \sum_i \left\langle \left\langle \frac{\mathbf{l}_{Ki}}{r_K^3} \cdot \frac{\mathbf{l}_{Li}}{r_L^3} \right\rangle \right\rangle_{E=0}, \quad (6)$$

the triplet Fermi contact (FC) contribution

$$J^{\text{FC}}(K,L) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{m_e} \right)^2 \frac{\gamma_K \gamma_L}{h} \left(\frac{8\pi}{3} \right)^2 \times \sum_i \left\langle \left\langle \delta(\mathbf{r}_K) \mathbf{s}_i; \delta(\mathbf{r}_L) \mathbf{s}_i \right\rangle \right\rangle_{E=0}, \quad (7)$$

and finally the triplet spin–dipole (SD) contribution

$$J^{\text{SD}}(K,L) = \frac{1}{3} \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e\hbar}{m_e} \right)^2 \frac{\gamma_K \gamma_L}{h} \times \sum_i \left\langle \left\langle \frac{3(\mathbf{s} \cdot \mathbf{r}_K) \mathbf{r}_{Ki} - r_{Ki}^2 \mathbf{s}_i}{r_K^5}; \frac{3(\mathbf{s} \cdot \mathbf{r}_L) \mathbf{r}_{Li} - r_{Li}^2 \mathbf{s}_i}{r_L^5} \right\rangle \right\rangle_{E=0}. \quad (8)$$

One notices the conceptual and computational simplicity of the relativistic expression compared to Ramsey's. In the rela-

tivistic case there are only three response equations to solve for a pair of nuclei whereas there are 13 in Ramsey's nonrelativistic theory (three for J^{OP} , one for J^{FC} because it is isotropic, and nine for J^{SD} since there are three spin components for each of the principal axes).

III. COMPUTATIONAL DETAILS

The relativistic calculations have been performed with the DIRAC program.¹⁷ In the electrostatic electron–nucleus interaction the finite nuclei were modeled by a Gaussian charge distribution.¹⁸ For the nonrelativistic calculations the DALTON program¹⁹ was used. The spin–spin coupling constant implementation¹² in DALTON uses the experimental value for the electronic *g*-factor, $g_e = 2.002\,319\,304\,386$, in the perturbing triplet operators. We rescaled these terms so that g_e is exactly equal to 2 as Dirac theory predicts.

In calculations involving the nuclear *g*-factor we used the following values: 5.585 694 for ¹H, 1.404 824 for ¹³C, −1.110 58 for ²⁹Si, −0.195 437 for ⁷³Ge, −2.094 56 for ¹¹⁹Sn, and 1.165 166 for ²⁰⁷Pb.

For the tetrahedral MH₄ molecules the experimental equilibrium distances, $R(\text{M–H})$, from Ref. 20 were used: 1.09, 1.48, 1.52, 1.70, and 1.75 Å going down the series. For trimethyl plumbane we used a geometry based on data from Refs. 21, 22: $R(\text{Pb–C}) = 2.250$ Å, $R(\text{Pb–H}) = 1.753$ Å, $R(\text{C–H}) = 1.086$ Å, $\theta(\text{C–Pb–C}) = 107.368^\circ$, $\theta(\text{C–Pb–H}) = 111.5^\circ$, and $\theta(\text{Pb–C–H}) = 111.6^\circ$.

The basis sets are uncontracted Gaussian-type, even-tempered²³ family basis sets. They are relativistically optimized using a modified version of GRASP.^{24,25} Tight *s*-functions and polarization functions were added. The details are given in Table I. The basis sets used for the methyl groups in trimethyl plumbane are Dunning DZ,^{26,27} completely uncontracted. The small component bases were generated using restricted kinetic balance. In the nonrelativistic calculations we used the relativistic large component bases.

IV. RESULTS AND DISCUSSION

We report both the usual coupling constant, J , and the reduced coupling constant, K ,²⁸

$$K(A,B) = \frac{2\pi}{\hbar \gamma_A \gamma_B} J(A,B). \quad (9)$$

TABLE II. Spin–spin coupling constants (in Hz) for SnH_4 with different two-electron integral approximations.

DHF	RPA	$J(^{119}\text{Sn}, ^1\text{H})$	$J(^1\text{H}, ^1\text{H})$
LL	LL	–2806.7	11.978
LL+SL	LL	–2636.3	9.5793
LL+SL	LL+SL	–2650.3	9.5824
LL+SL+SS	LL+SL	–2649.7	9.5774
LL+SL+SS	LL+SL+SS	–2650.2	9.5774

The latter only depends on the electronic environment and not on the nuclear magnetic moments and is therefore better suited for studying trends in a series of molecules with the same valence electronic structure.

A. Integral approximations

Full four-component relativistic calculations are computationally demanding. Thus, to overcome the storage bottleneck for two-electron integrals we use a direct scheme with an efficient integral screening.²⁹ The time consuming part is clearly the two-electron integral evaluation. For stannane we therefore tested several two-electron integral approximations by leaving out selected classes of two-electron integrals. The calculation of a coupling constant involves two steps. First, the Dirac–Hartree–Fock wave function must be determined, the DHF step, and second, the RPA equations are solved. DIRAC (Ref. 17) has a very flexible scheme for turning on and off evaluation of classes of integrals, and the two steps can be controlled independently. We show in Table II results for stannane using the different integral combinations that we have tested.

Including only two-electron integrals involving the large (LL) component basis (the crudest approximation) clearly overestimates the couplings. Including also the combined small–large (SL) integrals in the DHF step improves the two-bond coupling considerably. It is correct to within three significant figures, relative to the unapproximated calculation. However, the one-bond coupling is still off by 14 Hz. Most of that is recovered by including the SL integrals in the RPA part as well. When SS integrals are included in the DHF part but not the RPA, $J(^1\text{H}, ^1\text{H})$ is correct to five significant figures and $J(^{119}\text{Sn}, ^1\text{H})$ is correct to four figures. Thus this is a very good approximation and it eliminates all the expensive SS two-electron evaluation in the RPA part. We therefore decided to use this approximation for the calculations presented in Table V.

B. Basis set dependence

From nonrelativistic calculations it is well established that special basis set considerations are necessary to get reliable spin–spin coupling constants.^{30,31} Especially the Fermi contact operator requires tight s -functions in the basis to get converged couplings. In many cases the Fermi contact contribution is dominant and therefore of particular importance.

If we compare the operators in the response function for the relativistic case [Eq. (4)] with those from Ramsey's theory [Eqs. (6)–(8)] they appear at first sight rather different. It is therefore of interest to see if the relativistic four-

TABLE III. The effect of adding tight s -functions to the energy optimized basis set on the spin–spin coupling constants (in Hz) for CH_4 .

s -exponent	$\Delta j(^{13}\text{C}, ^1\text{H})^a$		$\Delta J(^1\text{H}, ^1\text{H})^a$	
	rel.	nonrel.	rel.	nonrel.
1.3×10^5	10.894	10.820	–2.4069	–2.4091
1.4×10^6	2.4533	2.4380	–0.6245	–0.6251
1.6×10^7	1.1704	1.1707	–0.2760	–0.2765

^aHere the Δ refer to the change in J as the result of adding an s -function.

component operator has the same needs for tight s -functions in the basis set. This is investigated by some test calculations on methane. We add the three tightest s -functions included in the final (see Table I) C and H basis sets one at a time and monitor the change in the couplings relative to the coupling from the preceding basis set. The results are shown in Table III.

One notes that there is an almost identical dependence on tight s -functions in the relativistic and nonrelativistic calculations. To explain this we recall that the relativistic interaction operator is proportional to [see Eqs. (1) and (3)]

$$\boldsymbol{\alpha} \cdot \frac{\mathbf{I} \times \mathbf{r}}{r^3}. \quad (10)$$

Since $\boldsymbol{\alpha}$ couples the small and large components [see Eq. (2)] the property matrix elements will involve a matrix element between the large and the small components of the spinor. Furthermore, in the nonrelativistic limit the large and the small components of the spinor are related by

$$\psi_i^S = \frac{1}{2m_e c} (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi_i^L. \quad (11)$$

Thus, the combination of Eqs. (10) and (2) shows that in the nonrelativistic limit the property matrix element is effectively proportional to a ψ_i^L, ψ_i^L matrix element of

$$\nabla \times \frac{\mathbf{I} \times \mathbf{r}}{r^3} = \left(\frac{3\mathbf{r}\mathbf{r} - \mathbf{I}r^2}{r^5} + \frac{8\pi}{3} \delta(\mathbf{r}) \right) \cdot \mathbf{I}, \quad (12)$$

that is, the sum of the FC and SD operators. This field gradient operator is in fact used to calculate the sum of the FC and SD integrals.¹² This explains why we see almost the same dependence on tight s -functions in the relativistic and nonrelativistic calculations, even though the operators look quite different at first sight.

C. Nonrelativistic results

In Table IV the nonrelativistic RPA results are presented. The four individual Ramsey contributions are shown explicitly. The one-bond couplings are clearly dominated by the Fermi contact contribution. For the two-bond couplings the situation is not that clear. In methane the FC contribution still dominates but for the other four molecules both the OD and OP contributions are numerical larger than the FC contribution. As is often the case for geminal H–H couplings the OD and OP contribution are almost of same size but have opposite sign. The results in Table IV are in good agreement with previous nonrelativistic RPA calculations.^{8,9}

TABLE IV. The nonrelativistic RPA contributions to the coupling constant (in Hz).

	$J(\text{M}, ^1\text{H})$					$J(^1\text{H}, ^1\text{H})$				
	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J	J^{OD}	J^{OP}	J^{SD}	J^{FC}	J
$^{13}\text{CH}_4$	0.24	1.44	-0.38	157.09	158.39	-3.50	3.68	0.51	-27.96	-27.27
$^{29}\text{SiH}_4$	-0.02	0.47	0.25	-245.32	-244.62	-2.37	2.27	0.07	-0.92	-0.95
$^{73}\text{GeH}_4$	-0.00	0.26	0.12	-110.79	-110.42	-4.85	4.31	0.06	-0.10	-0.58
$^{119}\text{SnH}_4$	-0.03	5.76	1.37	-1946.43	-1939.32	-4.81	3.29	0.01	2.71	1.19
$^{207}\text{PbH}_4$	0.02	-6.20	-1.03	1789.70	1782.50	-6.94	5.12	0.00	3.95	2.13

D. Relativistic results

The relativistic results (rel.) are shown in Table V together with the total nonrelativistic (n.r.) values from Table IV. Compared with the nonrelativistic results for the M–H coupling we see very small effects for methane and silane, as expected. For germane the relativistic coupling is increased by 12%. For stannane and plumbane the relativistic increase is more pronounced with 37% and 156%, respectively. The perturbative first-order spin–orbit corrections calculated previously by Kirpekar *et al.*^{7,9} tend to reduce the coupling constant, but at most by a few percent. We see a total relativistic effect in the MH_4 molecules which is much larger and of opposite sign, and we therefore conclude that the main relativistic effect is not due to spin–orbit but rather to the scalar relativistic contraction of the s -shells.

Also the H–H couplings are strongly affected by relativity going down the series of molecules. Since H is not very ‘‘relativistic’’ in itself there must be a large indirect relativistic effect from the heavy atom.

The largest absolute difference between the relativistic and nonrelativistic calculated OD contribution is less than 0.02 Hz and was observed for the two-bond coupling in PbH_4 . This excludes the OD term as a main contributor to the relativistic effect.

As mentioned in the introduction previous attempts to include relativity in calculations of coupling constants have used an atomic scaling factor, taking into account relativistic contractions of the inner s -shell of the heavy atom. We also tested this approach for the MH_4 molecules. We used the hydrogen-like relativistic correction factors tabulated by Pyykkö *et al.*³² The results (FCs) are shown in Table V. Compared to the full four-component relativistic results, the scaling works surprisingly well for the one-bond couplings but fails for the H–H couplings. From Table IV we see that the one-bond couplings are dominated by the FC contribution whereas the two-bond H–H couplings are not. Therefore one should not expect a scaling of only the FC contribution would work very well. This also agrees with a recent four-component relativistic study of NMR parameters for the hydrogen halides³³ for which scaling did not reproduce the relativistic results properly due to a large OP contribution to the H–X couplings. Furthermore the H–H coupling is not a coupling between two ‘‘heavy’’ nuclei and the relativistic effect is thus more indirect.

E. Comparison with experiment

It is well known from nonrelativistic calculations that inclusion of electron correlation is important for the accuracy

TABLE V. The reduced coupling constants (in $10^{19} \text{ T}^2 \text{ J}^{-1}$).

	$K(\text{M}, \text{H})$					$K(\text{H}, \text{H})$		
	n.r.	FCs ^a	rel.	$C \times \text{rel.}^b$	exp.	n.r. (=FCs) ^c	rel.	exp.
CH_4	52.4	52.6	52.6	43.5	40.0 ^d	-2.27	-2.27	-1.03 ^e
SiH_4	102.4	104.8	104.4	88.2	84.3 ^f	-0.08	-0.05	0.22 ^g
GeH_4	262.7	295.8	294.8	236.9	232 ^h	-0.05	0.64	0.64 ⁱ
SnH_4	430.5	580.9	588.3	458.8	429 ^j	0.10	0.80	1.27 ^e
PbH_4	711.4	1848.2	1819.0	1383.4	^k	0.18	3.62	
$\text{Pb}(\text{CH}_3)_3\text{H}$			1668.2 ^l		949 ^j			

^aScaling factor from Ref. 32.

^b C is the nonrel. ratio SOPPA/RPA from Refs. 8, 9.

^cThe n.r. and FC scaling results are identical since the scaling factor for H is so small that it does not change the nonrel. results to the accuracy shown in this table.

^dFrom Ref. 34.

^eFrom Ref. 35.

^fFrom Ref. 36.

^gFrom Ref. 37.

^hFrom Ref. 38.

ⁱFrom Ref. 39.

^jFrom Ref. 10.

^kAn estimate based on ratio of the calculated values for PbH_4 and $\text{Pb}(\text{CH}_3)_3\text{H}$ multiplied with the experimental value for the latter gives a value of $1035 \times 10^{19} \text{ T}^2 \text{ J}^{-1}$.

^lNone of the SS two-electron integrals were included in the calculation.

of the calculated coupling constants. Since no correlated relativistic four-component program is available for linear response calculations, we made a crude estimate based on the known importance of correlation in nonrelativistic calculations. We simply took the ratio of the coupling constant calculated within the nonrelativistic RPA and the correlated method SOPPA^{8,9} and multiplied our relativistic RPA results with this ratio (C in Table V). As seen from Table V the estimated couplings agree fairly well with experiment with a tendency to overestimate the couplings. This is of course a crude way to include correlation, assuming the same scaling in the relativistic and nonrelativistic calculations, but it at least shows that we are on the right track.

The couplings in plumbane has not been measured; instead the Pb–H coupling in trimethyl plumbane has been measured.¹⁰ However, as noted by Dalling and Gutowsky³ this coupling is undoubtedly somewhat smaller than the Pb–H coupling in plumbane. To see by how much, we did four-component relativistic calculation of the Pb–H coupling in trimethyl plumbane. This is a calculation using 1490 basis functions, so we decided on the basis of the integral test calculations (see Table II) to disregard the two-electron SS contribution. As shown in Table V we indeed find that the coupling in trimethyl plumbane is smaller by 8%. We used this calculation to get an estimate of the coupling in plumbane. Even though we get closer to experiment we are still considerably more off for the lead compound than for the other molecules.

Another consideration left out in this study is rovibronic corrections. They can be very important in comparisons with experiments because of the strong internuclear distance dependence of the couplings as shown in previous nonrelativistic studies on the same series of molecules.^{8,9}

V. CONCLUSIONS

We have demonstrated that four-component relativistic calculations of spin-spin coupling constants for larger molecules are feasible. The omission of SS two-electron integrals appears to be a promising route to reduce the computational cost. However, further investigations of a broader series of molecules need to be performed before it can be recommended in general.

We have shown that there is a similar dependence on and need for tight s -functions in the basis sets in the relativistic case as well as in the nonrelativistic case in order to get basis set converged results. This is explained examining the relativistic interaction operator in the nonrelativistic limit.

We find large relativistic effects for couplings in the molecules that contain a heavy atom, not only for couplings involving the heavy atom itself but also an indirect effect for the light atom two-bond couplings through the heavy atom. Even for a compound with a third row atom the relativistic increase in the coupling constant is as large as 10%. For all the calculated couplings in this article the relativistic correction to the reduced coupling constant is positive.

With a crude estimate of correlation we get close to experimental values, but tend to overestimate. The corrections are large and the need for a four-component relativistic cor-

related program to calculate spin-spin couplings for molecules with heavy atoms is evident.

We also find that scaling of the nonrelativistic FC term with atomic form factors which approximately includes the relativistic s -shell contraction give almost the same results as a full relativistic calculation for the one-bond couplings in the MH_4 molecules, while a similar approach for the hydrogen halides failed to reproduce the full relativistic result.³³ We believe that this difference hinges on the relative importance of the FC term for the two series of molecules.

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