

Relativistic study of nuclear magnetic shielding constants: hydrogen halides

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Abstract

Relativistic theory for calculating nuclear magnetic shielding constants is presented and applied to the proton shielding constant of hydrogen halides HX (X = F, Cl, Br, I). The spin-free relativistic (SFR) Hamiltonian is due to the no-pair theory of Sucher and Hess and is dealt with, together with the spin-orbit (SO) operator, by modifying the SO-UHF (unrestricted Hartree-Fock) method proposed previously. The SFR part introduces no new term to the shielding constant than those presented in the SO-UHF method. For the ¹H chemical shift, the SO effect of the heavy halogen is important, as reported previously, but the effect of the SFR term is small since it is essentially local on the heavy halogen atom.

1. Introduction

Relativistic effects are expected to be important for NMR chemical shifts of molecules including heavy elements [1], but research on this subject is so far limited [2–5]. Actually, no theoretical calculation of a heavy nucleus NMR chemical shift including full relativistic effects has been reported.

Among the relativistic effects, the spin-orbit (SO) effect has sometimes been treated separately from the others [6–8]. We have recently published the spin-orbit unrestricted Hartree-Fock (SO-UHF) method [9], which is a systematic method for calculating the SO effect on the nuclear magnetic shielding constant. This method is much easier to apply than the sum-over-state (SOS) perturbation method

[6], and has been applied to the halides of hydrogen, methyl [9], gallium, indium [10], silicon [11], aluminum [12] and others. The SO effects were shown to be so important that the chemical shifts of the complexes including heavier halogens such as bromine and iodine were not explained even qualitatively without the SO effects.

We report here a relativistic calculation of the nuclear magnetic shielding constant. We combine the spin-free relativistic no-pair theory of Sucher [13] and Hess [14,15] and the SO-UHF method [9] developed previously. The so-called mass-velocity (MV) and Darwin (DW) terms [16] are included in the former part, and the SO effect is dealt with by the latter method together with the external magnetic field.

We explain our method in some detail and apply it to the calculation of the ¹H shielding constants in the hydrogen halides, HX (X = F, Cl, Br, I). The conclusion is given in the last section.

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2. Method

Our zeroth-order Hamiltonian is the relativistic Hamiltonian which is spin-dependent and the external magnetic field is treated as a perturbation. The relativistic Hamiltonian is based on the no-pair theory presented by Sucher [13] and developed by Hess [14,15] for applications using conventional gaussian functions [17,18].

The relativistic no-pair Hamiltonian is divided into the spin-free part and the spin-dependent part: the former part, which we call the spin-free relativistic (SFR) part, involves, in addition to the non-relativistic terms, the so called MV and DW terms, and the latter the SO term. The calculation is performed in the Hartree–Fock level of approximation, and the SO interaction is calculated using the SO–UHF method proposed previously [9]. The effect of the external magnetic field is calculated, based on the finite perturbation method [19], in the framework of the SO–UHF method [9].

The relativistic no-pair Hamiltonian is defined in two different ways, one using the free-particle projectors [14] and the other using the external-field projectors [15], to exclude negative-energy eigenfunctions of the Dirac equation.

The spin-free Hamiltonian with the free-particle projectors used in this study is written as (Eq. (2.18) of Ref. [14])

$$\hat{h}_+ = \sum_i E_i + \sum_i V_{\text{eff}}(i) + \sum_{i<j} 1/r_{ij}, \quad (1)$$

with

$$V_{\text{eff}}(i) = - \left[A_i V_{\text{ext}}(i) A_i + \frac{A_i}{c^2 + E_i} p_i V_{\text{ext}}(i) p_i \frac{A_i}{c^2 + E_i} \right], \quad (2)$$

where

$$E_i = c^2 (p_i^2/c^2 + 1)^{1/2}, \quad (3)$$

$$A_i = [(c^2 + E_i)/2E_i]^{1/2}, \quad (4)$$

and the others are defined in Ref. [14]. The external potential $V_{\text{ext}}(i)$ in Eq. (2) represents the nuclear

attraction potential. The MV and DW terms arise from the first and second terms of Eq. (1), respectively. The spin-free no-pair Hamiltonian with external-field projectors is written as [15]

$$\hat{H}_+ = \sum_i E_i + \sum_i U_{\text{eff}}(i) + \sum_{i<j} 1/r_{ij}, \quad (5)$$

with

$$U_{\text{eff}}(i) = V_{\text{eff}}(i) + W_1(i) E_i W_1(i) + \frac{1}{2} W_1^2(i) E_i + \frac{1}{2} E_i W_1^2(i) \quad (6)$$

where $W_1(i)$ is defined in Ref. [15]. We neglect the projectors on the two-electron terms in both cases; the effects were shown to be small at least for the spin-free case [20]. It is recognized that the external field projectors give better results for molecular systems than the free-particle projectors.

Our zeroth-order Hamiltonian is written as

$$h^0 = h_+ + H_{\text{SO}} \quad (7a)$$

$$H^0 = H_+ + H_{\text{SO}}, \quad (7b)$$

where H_{SO} is the SO interaction operator. The SO term derived from the no-pair theory is different from the conventional Breit–Pauli form. However, we use in this study the conventional SO operator defined by

$$H_{\text{SO}} = \frac{1}{2c^2} \sum_N \sum_i Z_N \frac{\mathbf{L}_{Ni} \cdot \mathbf{S}_i}{r_{Ni}^3} - \frac{1}{2c^2} \sum_j \sum_{i \neq j} \frac{\mathbf{L}_{ij} \cdot \mathbf{S}_j + 2\mathbf{L}_{ji} \cdot \mathbf{S}_i}{r_{ij}^3} \quad (8)$$

just for simplicity, where \mathbf{L} and \mathbf{S} are the orbital and spin angular momentum operators, respectively. The Breit–Pauli SO operator overestimates the interaction compared to the SO operator of the no-pair theory [21]. Since H_{SO} involves spin-dependent operators, the relativistic wavefunction at the Hartree–Fock level becomes the generalized UHF wavefunction in which the orbital φ_k has a general spin factor as

$$\varphi_k = \phi_k^\alpha \alpha + \phi_k^\beta \beta. \quad (9)$$

However, using the property of the spin-linear operator, we have shown previously that the ordinary UHF method is also applicable to the calculations of the spin-orbit effects [9].

We now add the external magnetic Hamiltonian H_{ext} to our zeroth-order Hamiltonian

$$h = h_+ + H_{\text{SO}} + H_{\text{ext}} \quad (10a)$$

$$H = H_+ + H_{\text{SO}} + H_{\text{ext}} \quad (10b)$$

and calculate the response of a molecule to H_{ext} . The nuclear shielding constant is a property linear to the external magnetic field H_i and to the nuclear magnetic moment μ_{Ni} so that the magnetic Hamiltonian considered here is

$$H_{\text{ext}} = \sum_t H_t^{(1,0)} \cdot H_t + \sum_N \sum_t H_{Ni}^{(0,1)} \cdot \mu_{Ni} + \sum_N \sum_t \sum_u H_{Ntu}^{(1,1)} \cdot \mu_{Ni} H_u \quad (11a)$$

$$H_t^{(1,0)} = \frac{1}{2c} \sum_i (r_i \times p_i)_t + \frac{1}{c} \sum_i S_{it}, \quad (11b)$$

where $t, u = x, y, z$, and

$$H_{Ni}^{(0,1)} = \sum_i \frac{(r_{Ni} \times p_i)_t}{r_{Ni}^3} + \frac{1}{c} \sum_i \frac{3r_{Nit}(S_i \cdot r_{Ni}) - S_{it}r_{Ni}^2}{r_{Ni}^5} + \frac{3}{8} \pi \delta(r_{Ni}) S_{it} = H_{Ni}^{(0,1)}(\text{para}) + H_{Ni}^{(0,1)}(\text{SD}) + H_{Ni}^{(0,1)}(\text{FC}), \quad (11c)$$

$$H_{Ntu}^{(1,1)} = \frac{1}{2c^2} \sum_i \frac{r_i \cdot r_{Ni} \delta_{tu} - r_{it} r_{Ntu}}{r_{Ni}^3}. \quad (11d)$$

These formulae show that the relativistic magnetic shielding constant is expressed as [9]

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} + \sigma^{\text{SO}}(\text{SD}) + \sigma^{\text{SO}}(\text{FC}), \quad (12a)$$

with

$$\sigma_{Ntu}^{\text{dia}} = \langle \Psi(0) | H_{Ntu}^{(1,1)} | \Psi(0) \rangle, \quad (12b)$$

$$\sigma_{Ntu}^{\text{para}} = \frac{\partial}{\partial H_u} [\langle \Psi(H_i) | H_{Ni}^{(0,1)}(\text{para}) | \Psi(H_i) \rangle]_{H=0}, \quad (12c)$$

$$\sigma_{Ntu}^{\text{SO}}(\text{SD}) = \frac{\partial}{\partial H_u} [\langle \Psi(H_i) | H_{Ni}^{(0,1)}(\text{SD}) | \Psi(H_i) \rangle]_{H=0}, \quad (12d)$$

$$\sigma_{Ntu}^{\text{SO}}(\text{FC}) = \frac{\partial}{\partial H_u} [\langle \Psi(H_i) | H_{Ni}^{(0,1)}(\text{FC}) | \Psi(H_i) \rangle]_{H=0}, \quad (12e)$$

where $\Psi(0)$ and $\Psi(H_i)$ are the wavefunctions without and with the external magnetic field H_i and calculated by the SO-UHF method [9]. The abbreviations FC and SD stand for Fermi contact and spin-dipolar terms, respectively.

We note that the nuclear magnetic shielding constant σ in the relativistic Hamiltonian is expressed entirely in the same way as that taking only the SO effect under consideration [9]. In other words, the relativistic effects included further in the present study, namely the SFR terms, give no new direct terms to the magnetic shielding constant. These terms affect the shielding constant only through the changes in the electronic wavefunction.

In the following section, we show the results in the four different levels of approximations, which arise from combinations of the "relativistic spin-free" and "non-relativistic" and "with" and "without" the spin-orbit interaction, namely,

- level I: non-relativistic Hamiltonian
- level II: non-relativistic Hamiltonian with the SO term
- level III: relativistic spin-free no-pair Hamiltonian
- level IV: relativistic spin-free no-pair Hamiltonian with the SO term

equation (13).

The differences between different-level calculations serve the understanding as follows.

- level IV – level I: full relativistic effect
- level II – level I: SO effect in the non-relativistic environment
- level IV – level III: SO effect in the presence of the SFR terms
- level III – level I: SFR effects in the absence of the SO term

level IV – level II: SFR effects in the presence of the SO term

equation (14).

3. Proton magnetic shielding constants in hydrogen halides

We have reported previously [9] the importance of the SO effect on the proton magnetic shielding constants of the hydrogen halides HX (X = F, Cl, Br, I). Here, we study further the effect of the SFR terms like the MV and DW terms.

We use three different basis sets: set A is essentially the same as those used previously [9]: for hydrogen the Huzinaga–Dunning double-zeta set [22] plus p-FOBFs (first-order higher angular momentum basis functions) with the scale factor 1.2¹, and for halogens the double-zeta set from Huzinaga's book

¹ In the previous paper [9], the scale factor of the double-zeta hydrogen basis set, contracted as (31), was 1.2 for the inner three gaussian functions and 1.0 for the outer one gaussian function. The scale factors for the FOBFs were also 1.2 and 1.0 for the inner and outer ones, respectively. In the present calculations, the scale factor is 1.2 for all of the hydrogen basis.

[23] plus d-FOBFs for the valence p-functions. The FOBFs were shown to be useful for reducing the gauge origin dependence of the magnetic shielding constant [24]. Set B is the same as set A except that the primitive gaussians are used for hydrogen for both parent and FO basis functions. Set C is the same as set B except that the FOBFs are added to all inner core orbitals of halogens. The quality of the basis set is improved in the order set A, set B, set C. The gauge origin is located at the halogen atom since we already know that this choice gives more satisfactory results [24]. However, we also give the result obtained by putting the gauge origin on the hydrogen. The HX distances are 0.917, 1.274, 1.414 and 1.609 Å for X = F, Cl, Br and I, respectively [9]. As for the SO terms, we include only the one-electron term (first term of Eq. (8)).

Table I shows the energies of the molecules calculated at the relativistic and non-relativistic levels. The relativistic effect includes both SFR and SO terms. The energy lowering in the relativistic calculation has two sources. One is the variational nature of the present method; a better wavefunction gives a lower energy. The other is the positive-energy solution nature of the electronic system: mixing of a negative-energy part causes a lower solution. For

Table I
Total energies of the hydrogen halides at the non-relativistic and relativistic levels and with and without the spin-orbit effect (in hartree)^a

Compound	Non-relativistic Hamiltonian		Relativistic Hamiltonian			
	without SO	with SO	external-field projection		free-particle projection	
			without SO ^a	with SO	without SO	with SO
set A						
HF	-99.923782	-99.923791	-100.007006	-100.007015	-100.008251	-100.008259
HCl	-459.613725	-459.613821	-460.896406	-460.896505	-460.992157	-460.992256
HBr	-2570.759181	-2570.761474	-2591.877169	-2591.879260	-2600.088045	-2600.090123
HI	-6913.625697	-6913.636972	-6988.521599	-6988.530330	-7072.727802	-7072.734597
set B						
HF	-99.924118	-99.924127	-100.007351	-100.007360	-100.008596	-100.008604
HCl	-459.613889	-459.613990	-460.896582	-460.896683	-460.992333	-460.992431
HBr	-2570.759725	-2570.762046	-2591.877781	-2591.879900	-2600.088765	-2600.090876
HI	-6913.626456	-6913.637765	-6988.522378	-6988.531155	-7072.728156	-7072.736556
set C						
HF	-99.928139	-99.928154	-100.000434	-100.000451	-100.013161	-100.013176
HCl	-459.628636	-459.629882	-460.572729	-460.574020	-461.010239	-460.011610
HBr	-2570.876333	-2571.020921	-2582.875016	-2583.044099	-2600.604720	-2600.776878
HI	-6913.874413	-6915.969899	-6946.298906	-6949.229398	-7079.649666	-7083.482256

^a Total energy contribution of the SO term is calculated as a sum of the x, y and z contributions.

HF, the relativistic correction is small but it increases as the halogen atom becomes heavier. The energy lowering by the SFR term is larger than that by the SO terms. The total energy is always lower in the free-particle projection than in the external-field projection. The external-field projection is more relativistic for molecular systems than the free-particle projection, so that the mixing of the negative-energy part would be larger in the free-particle projection. The effect of uncontracting the hydrogen basis set is small, as expected, since hydrogen is the lightest atom. The addition of the derivative basis in Set C is helpful for maintaining the kinetic balance in the external field projection [25]; the effect of eliminating the negative-energy part in Set C is larger than the variational effect. In the free-particle projection, the addition of the derivative basis does not have such a clear meaning, so that an energy lowering results due to a variational effect.

Tables 2–5 show the proton magnetic shielding constant in hydrogen halides calculated at levels I to IV. Table 2, Tables 3 and 4 are for sets A, B and C,

respectively, with the gauge origin on the halogen. Table 4 is for set C with the gauge origin on hydrogen. The levels I and II results of Table 2 are slightly different from the previous ones [9], since there are slight differences in the basis set employed (see Footnote). The reference compound is hydrogen fluoride for the chemical shift calculations.

First we examine Table 2. Comparing the results of levels I and IV, we see that the relativistic effect is important for X = Br and I. The components σ^{dia} and σ^{para} are quite similar between levels I and IV and the most important relativistic effect is the SO effect arising predominantly through the FC term. The comparison between the results of levels I and II shows the SO effect using the non-relativistic orbitals, and the comparison between levels III and IV shows the SO effect in the relativistic environment. In both cases, the SO effect is large, but the magnitudes are different, showing a coupling between the SFR terms and the SO term. The comparison between levels I and III shows the effect of the SFR terms in the absence of the SO term: the effects are

Table 2

Proton magnetic shielding constants (ppm) and their analyses for hydrogen halides calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effects using set A and putting the gauge origin at the halogen

Compound	Without SO				With SO						δ^{exp}	
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}		δ^{cal}
							SD	FC	total			
non-relativistic Hamiltonian												
	level I				level II							
HF	16.05	11.51	27.56	0	16.05	11.51	0.01	0.17	0.18	27.75	0	0
HCl	16.92	12.99	29.91	-2.35	16.92	12.99	0.04	0.91	0.95	30.87	-3.12	-2.58
HBr	16.66	13.27	29.93	-2.37	16.67	13.27	0.18	5.33	5.51	35.45	-7.70	-6.43
HI	16.86	13.53	30.39	-2.83	16.91	13.52	0.40	16.29	16.69	47.11	-19.36	-15.34
Relativistic Hamiltonian (external-field)												
	level III				level IV							
HF	16.06	11.53	27.59	0	16.06	11.53	0.01	0.17	0.18	27.78	0	0
HCl	16.90	13.01	29.91	-2.32	16.90	13.01	0.04	0.92	0.96	30.88	-3.10	-2.58
HBr	16.59	13.33	29.92	-2.33	16.60	13.33	0.17	5.23	5.40	35.33	-7.55	-6.43
HI	16.68	13.60	30.28	-2.69	16.71	13.60	0.36	14.69	15.05	45.37	-17.59	-15.34
Relativistic Hamiltonian (free particle)												
	level III				level IV							
HF	16.06	11.53	27.59	0	16.06	11.53	0.01	0.17	0.18	27.78	0	0
HCl	16.90	13.01	29.91	-2.32	16.90	13.01	0.04	0.92	0.96	30.88	3.10	-2.58
HBr	16.59	13.33	29.92	-2.33	16.60	13.35	0.17	5.25	5.42	35.37	-7.59	-6.43
HI	16.70	13.65	30.35	-2.76	16.73	13.65	0.36	14.65	15.01	45.38	-17.60	-15.34

Table 3
Proton magnetic shielding constants (ppm) and their analyses for hydrogen halides calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effects using set B and putting the gauge origin at the halogen

Compound	Without SO				With SO							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}	δ^{cal}	
							SD	FC	total			
non-Relativistic Hamiltonian												
	level I				level II							
HF	15.89	11.91	27.80	0	15.89	11.91	0.01	0.16	0.17	27.97	0	0
HCl	16.82	13.07	29.89	-2.09	16.82	13.07	0.04	0.86	0.90	30.78	-2.81	-2.58
HBr	16.81	13.15	29.96	-2.16	16.82	13.15	0.18	4.96	5.14	35.11	-7.14	-6.43
HI	17.33	13.15	30.48	-2.68	17.37	13.13	0.39	15.15	15.54	46.05	-18.08	-15.34
Relativistic Hamiltonian (external-field)												
	level III				level IV							
HF	15.90	11.92	27.82	0	15.90	11.92	0.01	0.16	0.17	28.00	0	0
HCl	16.80	13.09	29.89	-2.07	16.80	13.09	0.04	0.86	0.90	30.80	-2.80	-2.58
HBr	16.70	13.23	29.93	-2.11	16.71	13.23	0.17	4.87	5.04	34.99	-9.99	-6.43
HI	17.08	13.27	30.35	-2.53	17.12	13.26	0.35	13.69	14.04	44.43	-16.43	-15.34
Relativistic Hamiltonian (free particle)												
	level III				level IV							
HF	15.90	11.92	27.82	0	15.90	11.92	0.01	0.16	0.17	28.00	0	0
HCl	16.80	13.09	29.89	-2.07	16.80	13.09	0.04	0.86	0.90	30.80	-2.80	-2.58
HBr	16.70	13.25	29.95	-2.13	16.71	13.25	0.17	4.89	5.06	35.03	-7.03	-6.43
HI	17.10	13.32	30.42	-2.60	17.13	13.31	0.35	13.65	14.00	44.44	-16.44	-15.34

Table 4
Proton magnetic shielding constants (ppm) and their analyses for hydrogen halides calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effects using set C and putting the gauge origin at the halogen

Compound	Without SO				With SO							δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}	δ^{cal}	
							SD	FC	total			
non-Relativistic Hamiltonian												
	level I				level II							
HF	15.84	11.94	27.78	0	15.84	11.94	0.02	0.17	0.19	27.96	0	0
HCl	16.79	13.00	29.79	-2.01	16.79	13.00	0.04	0.91	0.95	30.74	-2.78	-2.58
HBr	16.79	13.12	29.91	-2.13	16.80	13.12	0.17	5.09	5.26	35.18	-7.22	-6.43
HI	17.23	13.13	30.36	-2.58	17.27	13.12	0.40	16.51	16.91	47.29	-19.33	-15.34
Relativistic Hamiltonian (external-field)												
	level III				level IV							
HF	15.85	11.95	27.80	0	15.85	11.95	0.02	0.17	0.19	27.98	0	0
HCl	16.79	13.02	29.81	-2.01	16.79	13.02	0.04	0.93	0.97	30.77	-2.79	-2.58
HBr	16.68	13.13	29.81	-2.01	16.69	13.13	0.19	5.55	5.74	35.57	-7.59	-6.43
HI	16.95	13.15	30.10	-2.30	16.99	13.13	0.49	19.73	20.22	50.34	-22.36	-15.34
Relativistic Hamiltonian (free particle)												
	level III				level IV							
HF	15.85	11.95	27.80	0	15.85	11.95	0.02	0.17	0.19	27.98	0	0
HCl	16.79	13.02	29.81	-2.01	16.79	13.02	0.04	0.93	0.97	30.77	-2.79	-2.58
HBr	16.72	13.17	29.89	-2.09	16.72	13.17	0.19	5.69	5.79	35.78	-7.80	-6.43
HI	17.00	13.23	30.27	-2.47	17.04	13.21	0.53	21.54	22.07	52.32	-24.34	-15.34

Table 5

Proton magnetic shielding constants (ppm) and their analyses for hydrogen halides calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effects using set C and putting the gauge origin at hydrogen

Compound	Without SO				With SO						δ^{exp}		
	σ^{dia}	σ^{para}	σ^{tot}	δ^{cal}	σ^{dia}	σ^{para}	σ^{SO}			σ^{tot}		δ^{cal}	
							SD	FC	total				
non-Relativistic Hamiltonian													
	level I				level II								
HF	108.59	-78.50	30.09	0	108.59	-78.50	0.02	0.17	0.19	30.28	0	0	
HCl	141.95	-109.75	32.20	-2.11	141.95	-109.75	0.03	0.90	0.93	33.14	-2.86	-2.58	
HBr	249.15	-215.39	33.76	-3.67	249.16	-215.38	0.15	5.07	5.22	39.00	-8.72	-6.43	
HI	326.41	-292.95	33.46	-3.37	326.42	-292.94	0.36	16.47	16.83	50.30	-20.02	-15.34	
Relativistic Hamiltonian (external-field)													
	level III				level IV								
HF	108.59	-78.55	30.04	0	108.59	-78.55	0.02	0.17	0.19	30.23	0	0	
HCl	141.96	-110.00	31.96	-1.92	141.96	-110.00	0.04	0.92	0.96	32.92	-2.69	-2.58	
HBr	249.14	-216.74	32.40	-2.36	249.14	-216.73	0.17	5.53	5.70	38.10	-7.87	-6.43	
HI	326.35	-296.27	30.08	-0.04	326.36	-296.27	0.43	19.63	20.06	50.16	-19.93	-15.34	
Relativistic Hamiltonian (free particle)													
	level III				level IV								
HF	108.59	-78.55	30.04	0	108.59	-78.55	0.02	0.17	0.19	30.23	0	0	
HCl	141.96	-109.99	31.97	-1.93	141.96	-109.99	0.04	0.93	0.97	32.93	-2.70	-2.58	
HBr	249.16	-216.71	32.45	-2.41	249.16	-216.71	0.17	5.67	5.84	38.29	-8.06	-6.43	
HI	326.39	-296.44	29.95	0.09	326.39	-296.41	0.47	21.43	21.90	51.88	-21.65	-15.34	

small since here only the non-relativistic σ^{dia} and σ^{para} terms exist. The difference between levels II and IV results, which shows the SFR effects in the existence of the SO term, is also small. This is understood since the SFR effects like the MV and DW terms are local on the heavy halogen atom. The difference between the external-field projection and the free-particle projection in the shielding constant is small.

Next we examine the effect of uncontracting the hydrogen basis set by comparing the results shown in Tables 2 and 3. It is about 1.1 ppm for HI, which is small. The differences between the results in Tables 3 and 4 show the effects of the FOBFs added to the inner core orbitals of the halogens. The effect is to enlarge the FC term on the proton particularly at the relativistic level. As a result, the proton shielding constant becomes larger at level IV than at level II, in contrast to the result of sets A and B shown in Tables 2 and 3. This shows that the coupling between the SFR and SO terms increases in set C than

in sets A and B. By comparing Tables 4 and 5, we see the gauge-origin dependence for set C, which is about 2 ppm for the chemical shift.

Fig. 1 shows the correlation between theory and experiment for the proton chemical shifts of the hydrogen halides. The upper figure is for set A, the median for set B, and the lower one for set C. All are for the external-field projection and the gauge origin is on the halogen. Without the relativistic effects, the calculated shifts are far off the experimental values but with the relativistic effect the theory compares well with experiment: the SO effect overshoots and the SFR terms correct this overshooting. The halogen dependence of the chemical shifts in HX originates from the relativistic effect, particularly from the SO effect.

Thus, we could explain reasonably the proton chemical shift of the hydrogen halides using the relativistic method. However, a note is necessary here, i.e., we included only the one-electron term of the SO operator. Generally, the two-electron term

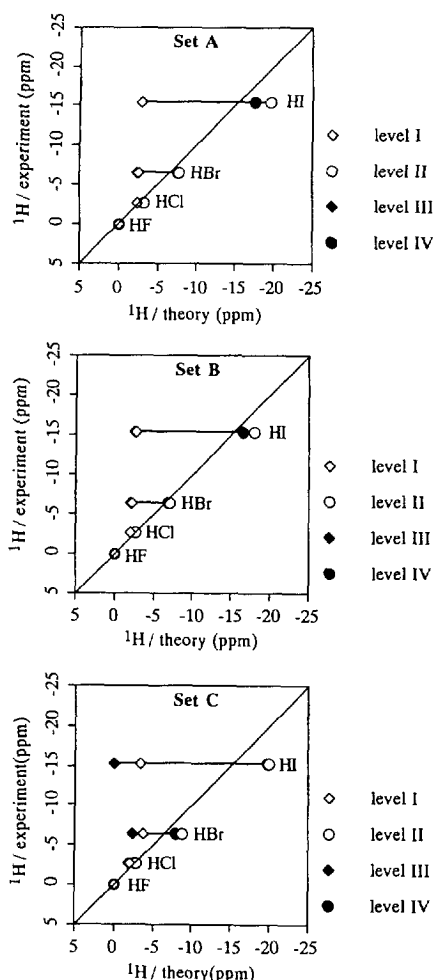


Fig. 1. Correlations between theory and experiment for the ^1H chemical shift in hydrogen halides. The relativistic calculations are due to the external-field projection and the gauge origin is on the halogen.

works to reduce the effect of the one-electron term. The effect of the electron correlation is also interesting. Such studies are now underway.

4. Concluding remarks

We have reported a method for the relativistic calculation of nuclear magnetic shielding constants and applied it to the proton shielding constant of hydrogen halides HX ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$).

The SFR Hamiltonian is due to the no-pair theory of Sucher and Hess and is dealt with, together with the SO operator by modifying the SO–UHF method reported previously [9]. The magnetic shielding constant is expressed in the same way as reported previously for including the SO effect in the framework of the SO–UHF method. The SFR term introduces no new terms in the shielding tensor calculations: it affects the shielding constant only through changes in the electronic wavefunction.

For the proton magnetic shielding constant and chemical shift of the hydrogen halides HX ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$), the SO effect of the attached heavy atom, Br and I, is important. The normal halogen dependence is explained only after including the SO effect, as reported previously [9]. The SFR terms, like the MV and DW terms, of the attached halogen are much less important than the SO term, since their effects are essentially local on the halogen.

Part of this study was presented at the ESF Workshop on the Calculation of NMR Parameters held in Helsinki [26]. In separate papers, we summarize relativistic calculations of the magnetic shielding constants of heavy nuclei attached to light and heavy elements like halogens.

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