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<**Abstract**>

Two expressions for nuclear magnetic shielding tensor components based on analytically differentiating the electronic energy of a system are presented. The first is based on a second-order Douglas-Kroll-Hess (DKH2) approach, in which the electronic states of the transformed Dirac Hamiltonian are correct to second order with respect to both the nuclear potential V and magnetic vector potential $\overrightarrow{A}$. The second expression is based on the method of Barysz-Sadlej-Snijders (BSS), in which the electronic states are completely correct with respect to V and correct to second order with respect to $\overrightarrow{A}$. The two approaches are applied to the calculation of nuclear magnetic shieldings of hydrogen halides with common gauge origins. Both methods yield similar results except for the shielding of nucleus I.

<**Results and Conclusion**>

Two analytical differentiation expressions for calculating nuclear magnetic shielding tensor components were derived at the coupled Hartree-Fock (CHF) level. The first approach is based on the second-order Douglas-Kroll-Hess (DKH2) method, and the second approach is based on the method of Barysz-Sadlej-Snijders (BSS). The second method is more exact than the first method. The two approaches were applied to the calculation of nuclear magnetic shieldings of hydrogen halides with common gauge origins. Each shielding of halogen and hydrogen atoms was computed using the two common gauge origins placed at the positions of halogen and hydrogen nuclei. The results are shown in Table I. The dependence of the computed shieldings on the gauge origin was small enough except for σ^{iso} of the proton in HI. Comparison of the results of present two approaches for hydrogen halide shieldings showed that the relativistic corrections of higher than second order are negligibly small except for the paramagnetic shielding of the I nucleus. The present results were found to be consistent with previously reported values for hydrogen halide shieldings, except for large disorepancies for the anisotropy $\Delta\sigma$ of proton shielding of HI compared to previous reports. Our calculated BSS-CHF value of $\Delta\sigma(\text{H})$ in HI is 26.55ppm (gauge center is on I) while the 4-RPA value of $\Delta\sigma(\text{H})$ in HI is -0.13ppm. The large anisotropy values for proton shieldings of HI shown in the present calculations are not thought to be due to error because the present values are similar for the two different approaches with the two different common geuge origins. Unfortunately, no experimental

values for the anisotropy of proton shielding in HI are available for verification. It is concluded that the present two expressions for calculating nuclear magnetic shielding yield self-consistent and reliable results.

TABLE I. Calculation of nuclear magnetic shielding constants σ^{iso} (in ppm) for HF, HCl, HBr, and HI by
the DKH2-CHF and BSS-CHF methods.

Molecule	Nucleus	Gauge origin	NR[a]	DKH2-CHF[b]	BSS-CHF[c]	4-RPA[d]
HF	F	F	413.5	417.1	417.0	423.3
	H	F	28.36	26.92	26.92	27.87
	F	H	413.5	412.6	412.6	423.3
	H	H	28.36	26.73	26.73	27.87
HCl	Cl	Cl	949.9	988.3	987.8	1020.1
	H	Cl	30.65	30.51	30.51	31.00
	Cl	H	949.9	983.3	982.8	1020.1
	H	H	30.65	30.09	30.09	31.00
HBr	Br	Br	2641.3	2982.1	2972.2	3224.6
	H	Br	31.01	35.45	35.46	36.08
	Br	H	2641.3	2978.6	2968.7	3224.6
	H	H	31.01	35.61	35.62	36.08
HI	I	I	4539.8	6303.4	6244.9	6768.4
	H	I	31.20	44.18	44.20	47.98
	I	H	4539.8	6301.1	6242.7	6768.4
	H	H	31.20	45.77	45.80	47.98

[a] Previous nonrelativistic results using GIAO's.
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[b] Present DKH2-CHF results.
[c] Present BSS-CHF results.
[d] Four-component relativistic random phase approximation results using GIAOs.
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