3P094

解析的微分による化学シフトの相対論的効果の計算

(北見工大) ○工藤 慶一、福井 洋之

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 off-diagonal block terms of the transformed Dirac Hamiltonian originating from the electrostatic nuclear attraction potential V and the magnetic vector potential $\overrightarrow{A}$ are diminished to second order with respect to the reciprocal of the velocity of light. The second expression is based on the method of Barysz and Sadlej (BS), in which the off-diagonal block terms originating from V in the transformed Dirac Hamiltonian are completely eliminated while the off-diagonal block vector potential terms are diminished to second order. The two approaches are applied to the calculation of nuclear magnetic shielding of hydrogen halides with common gauge origins. The results show that relativistic corrections of higher than second order are negligibly small except for the paramagnetic shielding of the I nucleus. The present calculations yield very different values for the anisotropy of proton shielding of HI compared to previous reports. Unfortunately, no experimental values for the anisotropy of proton shielding in HI are available for verification.

TABLE I. Calculation of nuclear magnetic shieldings (in ppm) for HF, HCl, HBr, and HI by the DKH2-CHF and BS-CHF methods.

Molecule	Nucleus	Gauge origin	NR[a]	DKH2-CHF[b]	BS-CHF[c]	BS-FPT-1[d]	4-RPA[e]
HF	F	F	413.5	419.9	418.5	418.1	423.3
	H	F	28.36	28.14	28.16	28.57	27.87
	F	H	413.5	416.4	420.6	418.1	423.3
	H	H	28.36	28.54	28.53	28.57	27.87
HCl	Cl	Cl	949.9	989.3	982.2	982.1	1020.1
	H	Cl	30.65	31.47	31.40	31.76	31.00
	Cl	H	949.9	984.6	991.4	982.1	1020.1
	H	H	30.65	31.77	31.86	31.76	31.00
HBr	Br	Br	2641.3	3008.6	2999.0	2978.6	3224.6
	H	Br	31.01	36.58	36.50	36.96	36.08
	Br	H	2641.3	3005.1	3002.1	2978.6	3224.6
	H	H	31.01	36.86	36.77	36.96	36.08
HI	I	I	4539.8	6455.6	6394.4	6077.0	6768.4
	H	I	31.20	45.73	45.57	49.62	47.98
	I	H	4539.8	6454.5	6330.7	6077.0	6768.4
	H	H	31.20	47.65	47.50	49.62	47.98

[a] Nonrelativistic results using GIAO's.
[b] Present DKH2-CHF results.
[c] Present BS-CHF results.
[d] Finite perturbation calculation results using the BS scheme and GIAOs.
[e] Four-component relativistic random phase approximation results using GIAOs.