Single-Excitation Configuration Interaction Calculations of Hyperfine Coupling Constants of Small π and σ Radicals

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Synopsis. Ab initio ROHF SCI calculations with Chipman's [5s2p/3†s] and [5s2p1d/3†s1p] basis sets, in which all singly-excited configurations are included, give hyperfine coupling constants of α-protons which are in satisfactory agreement with the experimental values.

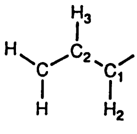
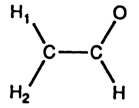
The hyperfine coupling constants (hfcc's) of free radicals have been calculated by a very wide range of theoretical methods.[1–11] Recently, Chipman examined various basis sets and suggested that the [4s2p/2s] double zeta Dunning basis set[12] is not appropriate for spin density calculations because of overcontraction in the outer core-inner valence region.[8] He stressed the importance of very high exponents of the s function in the Gaussian basis sets, and showed that the [5s2p/3†s] contracted Gaussian basis set performs well for spin density calculations of diatomic radicals. It is thus interesting to examine the hfcc's evaluated by singly-excited configuration interaction (SCI) calculation with Chipman's basis sets.[9,11] The SCI method includes all single excitations for describing important spin polarization effects and is expected to provide an economical and effective tool for the hfcc calculation of large polyatomic radicals. We have reported the SCI hfcc's of H_2O^+, CH_3, NH_2, CH_2CHCH_2, and CH_2CHO π radicals which are in satisfactory agreement with experiment.[11] In this note, the ROHF SCI calculations with the [5s2p/3†s] contracted basis set were carried out for 11 small radicals including σ radicals. The effect of polarization functions was also examined using six components of the Cartesian d functions. The orbital exponents of the d functions were determined by the following formula:[13]

$$\eta_d = 0.02Z^2,\ Z = 3,\cdots,10\ \text{(Li—Ne)}.$$

The exponent of the hydrogen p function was 0.75. In the present calculations, the experimental or optimized geometries were used.[14] The calculations were carried out on the NEWS-3460 workstation using the ABINIT88 program system formulated in our group.[11]

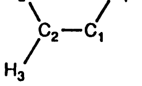
The calculated ROHF SCI isotropic hfcc's of π radicals are listed in Table 1, and those of σ radicals are in Table 2. In Table 1, hfcc's of five π radicals reported earlier[11] are also listed. Figures 1 and 2 show the correlation between the [5s2p1d/3†s1p] results and the experimental values for π and σ radicals, respectively. As shown in Table 1, the agreement between theory and experiment is fairly good for π radicals. However, the discrepancy between theory and experiment is large in the β-protons of π radicals. For σ radicals, the agreement with experiment is within about 20%, but discrepancies for the isotropic hfcc's of β-protons are larger than 30%. From Figs. 1 and 2, we see that the present theoretical values for β-protons tend to be smaller, in absolute value, than the experimental ones. An error

Table 1. Calculated Hyperfine Coupling Constants (in G) of π Radicals[a]

Radical	Atom	SCI/ [5s2p/3†s]	SCI/ [5s2p1d/3†s1p]	Expt[b]
H_2O^+ [c]	O	−24.7	−25.7	−29.7
	H	−26.9	−25.2	−26.1
CH_3[c]	C	30.8	26.5	27
	H	−27.2	−25.3	−25
NH_2[c]	N	9.0	9.0	9.9
	H	−25.0	−23.5	−23.9
NF_2	N	18.6	19.2	17
	F	78.4	69.4	60
 [c]	C_1	19.4	17.3	21.9
	C_2	−20.6	−19.3	−17.2
	H_1	−15.7	14.5	−14.8
	H_2	−15.0	−13.7	−13.9
	H_3	2.6	2.0	4.2
 [c]				
	H_1	−22.0	−20.6	−19.5
	H_2	−22.1	−20.8	−20.2
CH_3CH_2	C_α	35.0	30.9	29.5
	C_β	−15.6	−14.6	−13.6
	H_α	−27.0	−25.5	−22.4
	H_β	20.9	19.9	26.9
CH_3NH	N	11.5	11.0	13
	H_α	−24.7	−23.3	−22
	H_β	21.8	21.3	34
CH_3O	C	−14.5	−13.2	−15.6
	H	27.7	26.8	43.7

a) 1 G=10^{-4} T. b) Ref. 15. c) Ref. 11.

Table 2. Calculated Hyperfine Coupling Constants (in G) of σ Radicals

Radical	Atom	SCI/ [5s2p/3†s]	SCI/ [5s2p1d/3†s1p]	Expt[a]
NO_2	N	48.5	53.3	52.3
HCO	C	159.3	154.4	130.5
	H	112.3	121.0	126.3
	C_1	132.4	124.8	107.6
	C_2	−8.0	−5.2	−8.6
	H_1	8.1	10.9	13.4
	H_2	43.0	42.3	65
	H_3	25.4	23.4	37
H_2CN	C	−30.6	−28.3	−28.9
	N	8.0	7.0	10.2
	H	67.0	64.2	87.3
H_2CC^-	H	46.1	44.2	58
H_2BO	B	−21.9	−19.5	−31.0
	H	53.4	50.5	132.9
H_2CO^+	C	−30.1	−28.4	−38.8
	H	75.3	76.4	132.7

a) Ref. 15.

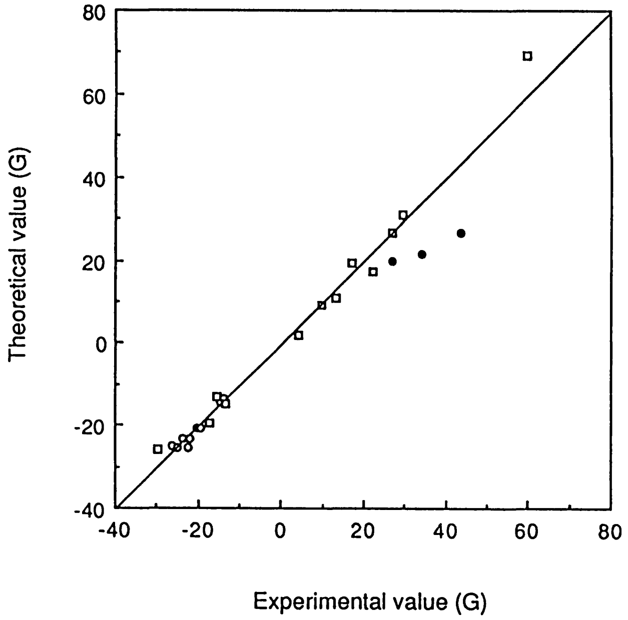


Fig. 1. Comparison between experimental and theoretical (SCI/[5s2p1d/3†s1p]) values of the hfcc's for α-proton (○), β-proton (●), and other atoms (□) of π radicals.

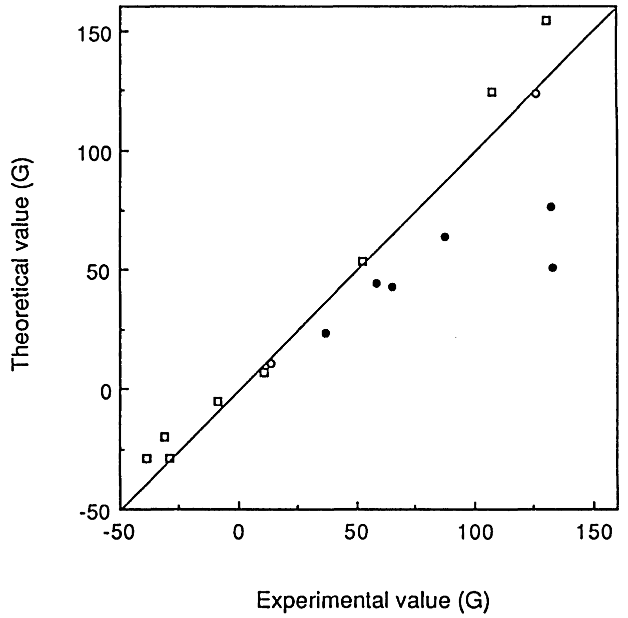


Fig. 2. Comparison between experimental and theoretical (SCI/[5s2p1d/3†s1p]) values of the hfcc's for α-proton (○), β-proton (●), and other atoms (□) of σ radicals.

Table 3. Hyperfine Coupling Constants (in G) of H_2CN[a]

Basis set	Method	^{13}C	^{14}N	^{1}H
[8s4p1d/6s1p][b]	MR-SDCI	4.7	−25.3	69.9
[4s2p1d/2s1p][c]	SCI	6.7	−25.0	57.9
[6s3p1d/4s1p][d]	SCI	7.9	−25.5	59.4
[7s4p4d1f/5s2p1d][d]	QCISD(T)	9.3	−27.8	75.4
Present				
[5s2p/3†s]	SCI	8.0	−30.6	67.0
[5s2p1d/3†s1p]	SCI	7.0	−28.3	64.2
[5s2p/3†s]	2R-SCI	6.9	−30.2	71.1
Expt[c]		10.2	(−)28.9	87.3

a) Ref. 14. b) Ref. 1. c) Ref. 15. d) Ref. 9.

Table 4. Hyperfine Coupling Constants (in G) of H_2CO^+[a]

Basis set	Method	^{17}O	^{13}C	^{1}H
[8s4p1d/6s1p][b]	MR-SDCI	−14	−24	80
[4s2p1d/2s1p][c]	CCSD	−21	−37	100
[4s2p/2s][d]	SAC-CI	−13.3	−28.8	117.1
STO p(GTO)[e]	SAC-CI	−19.9	−29.8	119.4
Present				
[5s2p/3†s]	SCI	−21.2	−30.1	75.3
[5s2p1d/3†s1p]	SCI	−19.5	−28.4	76.4
[5s2p/3†s]	2R-SCI	−17.3	−29.9	91.8
Expt[f]			(−)38.8	132.7

a) Ref. 14. b) Ref. 1. c) Ref. 6. d) Ref. 4. e) Ref. 5. f) Ref. 15.

as large as 30% found for the β-protons is attributed primarily to the missing effects of electron correlation.[9,10] In order to consider this point partly, the two-reference SCI calculations were performed for the H_2CN and H_2CO^+ radicals (Tables 3 and 4). The second reference configuration corresponds to the π–π^* pair (double) excitation. For the H_2CN radical, the proton hfcc is improved by the 2R-SCI calculation; the 2R-SCI result is almost same as the QCISD(T) value.[10] However, the theoretical values are still smaller than the experimental value. For the H_2CO^+ radical, the 2R-SCI calculation yields fairly good results compared with the twelve reference SDCI calculation,[1] although the theoretical values explain only 70% of the experimental values. As shown in Tables 3 and 4, the isotropic hfcc of β-protons were improved by including a part of three-electron excitation. However, the discrepancies from experimental values are still large, and it is necessary to include higher order excitations in the wave function to obtain more accurate hfcc's of β-protons.

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