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Calculation of hfs Coupling Constants by the Roothaan "Plus" Configuration Interaction Method within the INDO Approximation

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A new set of parameters, relating hfs coupling constants to the spin densities calculated by the RHF+CI method, within the INDO approximation, is given for ^{1}H, ^{13}C, ^{14}N, ^{17}O, ^{19}F. On the whole the results, obtained for a homogeneous sample of organic radicals, are in better agreement with experimental ones, as compared with UHF method.

Key words: hfs constants – Organic radicals – RHF+CI method

1. Introduction

The hyperfine interaction between electron and nuclear magnetic moments is related to the spin density at the magnetic nucleus, that is the hyperfine coupling constants depend on a local property of the wavefunction and its accurate calculation is an exceedingly difficult task. The *ab initio* calculations, requiring a heavy amount of computing time, give in general scarcely reliable results. In this view the semiempirical methods have been more widely used. One of the most satisfactory is the INDO (Intermediate Neglect of Differential Overlap) method [1, 2], including all valence electrons. The open shell wavefunction is usually calculated within the "unrestricted" Hartree–Fock (UHF) approximation, so that this wavefunction does not represent pure spin states [3, 4]. We can obtain them through the application of an annihilation operator, which removes all or at least the most contaminating spin components, that is the quartet contaminating the doublet ground state [5]. However, the projected unrestricted wavefunctions often do not improve qualitatively the spin distribution of the radical. In general only the

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smallest proton hyperfine splitting (hfs) coupling constants are quantitatively improved.

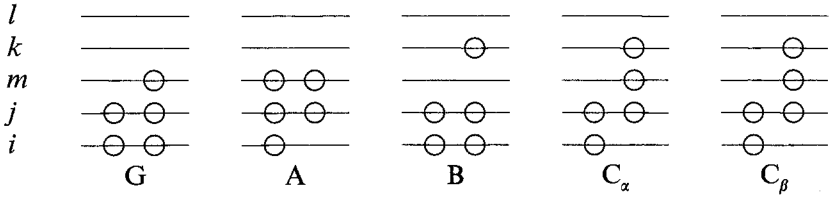
Alternatively the restricted wavefunction represents the pure spin state [6]. In this case the combined use of configuration interaction (CI) is required to obtain π odd electron density at the nuclei, and in general to obtain negative spin densities.

In a previous paper [7] a first comparison of the results of the two methods was performed for 1,3-dinitrobenzene and 3,5-dinitropyridine anion radicals. Recently Klimo and Tinŏ [8] reported the results obtained by the RHF + CI method on a set of nine small radicals.

In the present work we extend the test to a large variety of organic radicals to verify whether the RHF + CI INDO wavefunctions give reliable spin distributions. We also compare the present results with the corresponding ones calculated by the UHF method [2, 5]. The parameters which translate spin densities into hfs coupling constants are obtained for ^{1}H, ^{13}C, ^{14}N, ^{17}O, and ^{19}F through the least square fitting between calculated spin densities and experimental hfs coupling constants. The corresponding parameters related to the UHF wavefunctions were previously given by Pople and coworkers [2, 5].

2. Method

For radicals with one unpaired electron in a nondegenerate level in the ground state there are four types of singly excited configurations, denoted in the literature as A, B, C_α, and C_β [9].



The corresponding wavefunctions are:

$$^{2}\psi_{\mathrm{G}} = |\varphi_1\bar{\varphi}_1 \cdots\cdots\cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m|$$

$$^{2}\psi_{\mathrm{A}} = |\varphi_1\bar{\varphi}_1 \cdots \varphi_i\bar{\varphi}_m \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m|$$

$$^{2}\psi_{\mathrm{B}} = |\varphi_1\bar{\varphi}_1 \cdots\cdots\cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_k|$$

$$^{2}\psi_{\mathrm{C}_\alpha} = 1/\sqrt{2}\{|\varphi_1\bar{\varphi}_1 \cdots \varphi_i\bar{\varphi}_k \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| + |\varphi_1\bar{\varphi}_1 \cdots \varphi_k\bar{\varphi}_i \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m|\}$$

$$^{2}\psi_{\mathrm{C}_\beta} = 1/\sqrt{6}\{|\varphi_1\bar{\varphi}_1 \cdots \varphi_i\bar{\varphi}_k \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| - |\varphi_1\bar{\varphi}_1 \cdots \varphi_k\bar{\varphi}_i \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_m| + 2|\varphi_1\bar{\varphi}_1 \cdots \varphi_i\bar{\varphi}_m \cdots \varphi_{m-1}\bar{\varphi}_{m-1}\varphi_k|\}$$

Matrix elements between these configurations are available in Ref. [9]. Only the C_β configurations interact directly with the ground one, and give first order contributions to the spin density. However the configurations A, B, and C_α, which interact with the C_β one, give second order contributions. In this view only the C_β configurations have been taken into account for the complete set of the considered radicals. To test the validity of this assumption, in the case of small radicals, the results are compared with calculations including all the singly excited configurations. Among the C_β configurations only the ones having the largest matrix elements with ground configuration, to a maximum of 80 have been included in the CI calculation. The programme used for the calculation will be sent to QCPE.

3. Calculation

A large variety of π and σ radicals, composed of first row atoms and representative of different molecular environments, were considered. Owing to the lack of experimental geometries the following criteria were adopted for defining the geometrical parameters. The geometries of the small and middle size radicals were obtained by

Table 1. Optimized geometrical parameters for AB, A_2B, ABC, A_3B, and A_2BC radicals

Radical	Type	$\overline{AB}$ (Å)	$\overline{BC}$ (Å)	$\widehat{ABC}$	$\widehat{ABA}$
CN	AB	1.17			
NH_2	A_2B	1.07			105.0
CO_2^-		1.28			136.0
NO_2		1.19			138.0
NO_2^{--}		1.29			119.0
NF_2		1.23			106.0
Me_2N^a		1.38			119.0
CCH	ABC	1.20	1.10		180.0
HBO^-		1.22	1.36		129.0
HCN^-		1.18	1.22		134.0
HCO		1.12	1.22		131.0
NCO		1.21	1.28		180.0
FCO		1.32	1.23		129.0
FOO		1.19	1.19		110.0
CH_3	A_3B	1.10			120.0
NH_3^+		1.08			120.0
CF_3		1.325			112.5
Me_3c		1.44			120.0
H_2CN	A_2BC	1.12	1.26	124.0	112.0
H_2CO^-		1.13	1.31	124.0	112.0
H_2CF		1.11	1.325	115.0	120.0
F_2CH		1.325	1.10	115.0	110.0
$MeNO_2^-$		1.26	1.42	118.0	124.0
Me_2CH		1.44	1.13	116.5	127.0
Me_2NH^+		1.40	1.08	116.0	128.0

[a] Me : CH_3 ; CH = 1.13 Å and $\widehat{HCH}$ = 106.4°. The rotations of CH_3 group were always taken into account.

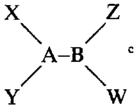
minimizing the RHF total energy with respect to the relevant geometrical bond lengths and bond angles. The optimized geometries are reported in Tables 1–3. For pyridine [10], nitrobenzene [11], 1,3- and 1,4-dinitrobenzene [12, 13], 3,5-dinitropyridine [14], *ortho*- and *para*-benzosemiquinone [15, 16] anion radicals and mono-fluoroacetamide [17] radical the experimental geometries of the corresponding neutral molecules were assumed. For difluoroacetamide radical the geometry of mono-fluoroacetamide was assumed. Optimized INDO geometries for pyrimidine, pyrazine, pyridazine neutral molecules [18], and benzyl radical [19] were adopted. For vinyl radical the geometry of Ref. [20] was assumed.

Model geometries were used for phenyl radical and *sym*-tetrazine, benzonitrile, phthalonitrile, isophthalonitrile, terephthalonitrile, 2-fluoropyridine anion radicals. The following bond lengths were used: C=C: 1.39; C=N: 1.34; C–F: 1.33; C≡N: 1.20; C–C(CN): 1.37; C–H: 1.085 Å, with all bond angles of 120° [21].

4. Results and Discussion

The spin distributions of the organic radicals are dependent on the geometrical parameters, as shown for example for benzyl [19]. The choice of a model geometry

Table 2. Optimized geometrical parameters for CX_2–CY_2Z and AXY–BZW radicals

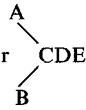
CX_2–CY_2Z	$\overline{CC}$	$\overline{CX}$	$\overline{CY}$	$\overline{CZ}$	$\widehat{XCC}$	$\widehat{YCC}$	$\widehat{ZCC}$	$\widehat{YCZ}$	φ[a]
CH_2–CH_3	1.42	1.11	1.13	—	123.0	112.4	—	—	4.3
CH_2–CH_2F	1.44	1.11	1.13	1.37	123.0	113.0	113.0	105.7	0.0
CH_2–CF_2H	1.44	1.11	1.35	1.13	123.0	113.0	113.0	105.7	0.0
CH_2–CF_3	1.44	1.11	1.35	—	122.0	113.6	—	—	0.0
CF_2–CF_3[b]	1.46	1.33	1.35	—	118.9	113.2	—	—	37.1
 [c]	$\overline{AB}$	$\overline{AX}$	$\overline{AY}$	$\overline{BZ}$		$\widehat{XAB}$	$\widehat{YAB}$	$\widehat{ABZ}$	
NH_2–NH_2^+	1.29	1.07	—	—		120.0	—	—	
NHMe–NH_2^+	1.29	1.07	1.40	1.07		116.0	122.0	120.0	
NMe_2–NH_2^+	1.29	1.42	—	1.07		120.0	—	120.0	
NHMe–$NHMe^+$									
trans	1.29	1.07	1.42	—		118.0	124.0	—	
cis	1.29	1.07	1.40	—		116.0	124.0	—	
NMe_2–NMe_2^+	1.29	1.42	—	—		122.0	—	—	
CH_2–CO_2^-	1.41	1.11	—	1.32		125.0	—	119.0	
CH_2–OH[c]	1.34	1.11	—	1.04		120.0	—	109.0	
CH_2–OMe[c]	1.34	1.11	—	1.38		120.0	—	108.0	
CMe_2–OH[d]	1.34	1.46	—	1.04		116.0	—	109.0	

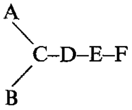
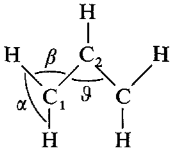
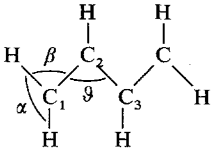
[a] $(180-\varphi)$ is the angle between the C–C bond and the bisector of $\widehat{XCX}$ angle.

[b] Ref. [22].

[c] Planar system.

[d] Non planar system: $\widehat{XAY} = 117.7$, the bond OH eclipsing the bisector of $\widehat{XAY}$ angle.

Table 3. Optimized geometrical parameters for  $A(B)C\text{-}DEF$, allyl and butadiene anion radicals

	$\overline{CA}$	$\overline{CB}$	$\overline{CD}$	$\overline{DE}$	$\overline{EF}$	$\widehat{ACD}$	$\widehat{BCD}$
H_2CCN	1.11	—	1.34	1.23	—	121.0	—
H_2CCCH	1.11	—	1.37	1.23	1.09	123.0	—
MeHCCN	1.13	1.44	1.34	1.24	—	119.0	123.0
H_2CCCMe	1.11	—	1.36	1.24	1.42	123.0	—
	$\overline{C_1C_2}$	$\overline{C_2C_3}$	$\overline{C_1H}$	$\overline{C_2H}$	ϑ	α	β
	1.37	—	1.11	1.12	126.0	112.0	124.0
	1.38	1.40	1.12	1.13	131.0	112.0	124.0

is troublesome for small radicals, that is for the systems showing more strongly such a dependence: so we have optimized the geometries whenever possible (see Tables 1–3). On the other hand the spin distributions of large rigid radicals are less dependent on small variations of bond lengths and bond angles, and in this view model geometries or the experimental geometries of the corresponding neutral molecules can be reasonably assumed.

The entries in Tables 4–8 are the calculated and experimental hfs coupling constants a_N, associated to the magnetic nuclei of the considered radicals. The theoretical expression of a_N, in the framework of INDO method, is given by the following relationship:

$$a_N = [(4\pi/3) g\beta\gamma_N\hbar\langle s_z\rangle^{-1}|\phi_{s_N}(r_N)|^2]\,\rho_{s_N s_N} \qquad [1]$$

where $\rho_{s_N s_N}$ is the spin density associated to the s-orbital of atom N. The quantity in brackets on the right hand of Eq. (1) is a constant for each type of magnetic nucleus. This quantity includes all fundamental constants with the exception of the valence s-function of atom N, $|\phi_{s_N}(r_N)|^2$. Our procedure for determining $|\phi_{s_N}(r_N)|^2$ involves recognizing the linear relation between a_N and $\rho_{s_N s_N}$. The values of these quantities which give the best fit between the observed a_N and the calculated $\rho_{s_N s_N}$ in the least square sense are collected in Table 9, where they are compared with the

Table 4. Observed and calculated hfs coupling constants for ^1H

Radical	Atom	a_N (gauss)		Ref.
		Calcd.	Exptl.	
CCH		34.5	(+) 16.1	[23]
CH_3		− 17.4	(−) 23.0	[24]
vinyl	CH	13.2	(+) 16.0	[23]
	CH_2			
	cis	72.0	(+) 68.0	[23]
	trans	34.8	(+) 34.0	[23]
ethyl	CH_2	− 15.3	(−) 22.4	[24]
	CH_3	42.7	(+) 26.9	[24]
allyl	CH_2			
	trans	− 9.2	(−) 13.9	[24]
	cis	− 9.4	(−) 14.8	[24]
	CH	1.6	(+) 4.1	[24]
trans butadiene$^-$	CH_2	− 6.4	(−) 7.6	[25]
	CH	− 2.1	(−) 2.8	[25]
$CH(CH_3)_2$	CH	− 14.1	(−) 22.1	[24]
	CH_3	35.4	(+) 24.7	[24]
$C(CH_3)_3$		31.3	(+) 22.7	[24]
phenyl	2	15.7	(+) 19.5	[26]
	3	6.5	(+) 6.5	[26]
benzyl	2	− 1.9	(−) 5.1	[27]
	3	− 0.2	(−) 1.8	[27]
	4	− 1.5	(−) 6.1	[27]
	CH_2	− 12.6	(−) 16.4	[27]
CH_2CCH	CH	− 6.3	(−) 12.6	[28]
	CH_2	− 13.7	(−) 19.0	[28]
CH_2CCCH_3	CH_2	− 12.6	(−) 18.6	[28]
	CH_3	16.6	(+) 12.4	[28]
HCN^-		167.3	(+)136.4	[29]
H_2CN		71.8	(+) 91.2	[29]
CH_2CN		− 10.6	(−) 21.2	[28]
CH_3CHCN	CH	− 10.5	(−) 20.5	[28]
	CH_3	26.0	(+) 23.1	[28]
NH_2		− 15.5	(−) 23.9	[30]
NH_3^+		− 18.7	(−) 25.9	[31]
$(CH_3)_2N$		28.5	(+) 27.4	[32]
$(CH_3)_2NH^+$	NH	− 15.4	(−) 22.7	[33]
	CH_3	27.7	(+) 34.3	[33]
hydrazine$^+$		− 11.1	(−) 11.0	[34]
methylhydrazine$^+$	1	− 11.8	(−) 12.2	[35]
	2	− 8.5	(−) 8.5	[35]
	2′	− 9.3	(−) 8.9	[35]
	CH_3	14.3	(+) 14.4	[35]
1,1-dimethylhydrazine$^+$	NH	− 8.1	(−) 6.9	[36]
	CH_3	13.3	(+) 14.4	[36]
1,2-dimethylhydrazine$^+$	*cis* NH	− 10.3	(−) 10.8	[35]
	CH_3	− 12.9	(+) 12.6	[35]
1,2-dimethylhydrazine$^+$				
trans	NH	− 9.7	(−) 9.8	[35]
	CH_3	11.1	(+) 12.2	[35]
tetramethylhydrazine$^+$		10.2	(+) 12.7	[37]
pyrimidine$^-$	2	− 1.3	(−) 1.3	[38]
	4	− 5.7	(−) 9.8	[38]
	5	+ 0.5	(+) 0.7	[38]
pyridine$^-$	2	− 2.9	(−) 3.6	[38]
	3	− 0.9	(−) 0.8	[38]
	4	− 5.2	(−) 9.7	[38]
pyrazine$^-$		− 2.2	(−) 2.6	[39]
pyridazine$^-$	3	− 0.7	(−) 0.2	[39]
	4	− 2.7	(−) 6.5	[39]
tetrazine$^-$		− 0.5	(−) 0.2	[39]
benzonitrile$^-$	2	− 2.0	(−) 3.6	[40]
	3	− 0.7	(−) 0.3	[40]
	4	− 3.9	(−) 8.4	[40]
terephthalonitrile$^-$		− 1.3	(−) 1.6	[40]
phthalonitrile$^-$	3	− 0.3	(−) 0.4	[40]
	4	− 1.9	(−) 4.1	[40]
isophthalonitrile$^-$	2	0.1	(+) 1.4	[40]
	4	− 3.8	(−) 8.3	[40]
	5	− 0.1	(−) 0.1	[40]
HBO^-		75.5	(+) 94.0	[41]
HCO		85.9	137.0	[42]
CH_2O^-		− 10.8	(−) 14.3	[43]
CH_2OH	CH_2			
	trans	− 16.1	(−) 18.5	[44]
	cis	− 15.7	(−) 17.7	[44]
	OH	− 2.6	(−) 2.2	[44]
CH_2OCH_3	*trans*	− 15.7	(−) 17.1	[44]
	cis	− 16.0	(−) 18.4	[44]
	CH_3	− 0.2	(−) 2.1	[44]
$(CH_3)_2COH$	CH_3	22.6	(+) 19.5	[45]
$CH_2CO_2^-$		− 12.5	(−) 21.2	[45]
$CH_3NO_2^-$		16.6	(+) 12.0	[46]
nitrobenzene$^-$	2	− 0.5	(−) 3.3	[47]
	3	0.2	(+) 1.1	[47]
	4	− 0.7	(−) 4.0	[47]
m-dinitrobenzene$^-$	2	− 0.4	(−) 3.0	[48]
	4	− 3.0	(−) 4.1	[48]
	5	− 0.1	(−) 1.1	[48]
p-dinitrobenzene$^-$		− 1.2	(−) 1.1	[49]

Table 4—*cont.*

		a_N(gauss)					a_N(gauss)		
Radical	Atom	Calcd.	Exptl.	Ref.	Radical	Atom	Calcd.	Exptl.	Ref.
3,5-dinitro-					CH_2CFH_2	CH_2	− 15.1	(−) 22.2	[54]
pyridine$^-$	2	− 3.9	(−) 4.6	[50]		CFH_2	37.7	(+) 27.9	[54]
	4	− 1.0	(−) 3.4	[50]	CH_2CF_3		− 16.1	(−) 23.8	[54]
o-benzosemi-					CH_2CF_2H	CH_2	− 15.9	(−) 23.4	[55]
quinone$^-$	3	− 1.4	(−) 3.7	[51]		CF_2H	32.1	(+) 12.3	[55]
	4	− 1.0	(−) 1.0	[51]	2-fluoropyridine	3	− 0.7	(−) 3.7	[56]
p-benzosemi-						4	− 5.4	(−) 8.3	[56]
quinone$^-$		− 1.5	(−) 2.4	[52]		5	− 0.3	(−) 1.1	[56]
CH_2F		− 2.7	(−) 21.1	[53]		6	− 3.2	(−) 4.6	[56]
CHF_2		29.4	(+) 22.2	[53]					

Table 5. Observed and calculated hfs coupling constants for ^{13}C

		a_N (gauss)					a_N (gauss)		
Radical	Atom	Calcd.	Exptl.	Ref.	Radical	Atom	Calcd.	Exptl.	Ref.
CH_3		40.7	(+) 38.3	[57]	$(CH_3)_2COH$	COH	66.3	(+) 65.1	[45]
vinyl	CH	126.6	(+)107.6	[57]		CH_3	− 3.4	(−) 5.4	[45]
	CH_2	− 7.8	(−) 8.6	[57]	$CH_2CO_2^-$	CH_2	31.6	(+) 32.1	[45]
ethyl	CH_2	33.4	(+) 39.1	[57]		CO_2^-	− 5.6	(−) 13.9	[45]
	CH_3	− 10.8	(−) 13.6	[57]	*p*-dinitro-				
CN		168.7	(+)210.0	[58]	benzene$^-$	1	6.7	(+) 2.1	[49]
HCN^-		186.6	(+) 74.7	[29]		2	0.7	(+) 0.6	[49]
pyrazine$^-$		0.4	(+) 2.9	[39]	*o*-benzosemi-				
benzonitrile$^-$	CN	− 1.4	(−) 6.1	[40]	quinone$^-$	1	0.1	(+) 2.0	[61]
terephthalo-						3	2.2	(+) 3.3	[61]
nitrile	1	6.6	(+) 8.8	[40]		4	1.3	(+) 2.6	[61]
	2	0.6	(+) 2.0	[40]	*p*-benzosemi-				
	CN	− 2.3	(−) 7.8	[40]	quinone$^-$	1	− 0.3	(−) 0.4	[62]
HCO		155.2	(+)135.0	[59]		2	1.9	(+) 0.6	[63]
CO_2^-		155.1	(+)147.9	[60]	FCO		219.8	(+)286.6	[59]
CH_2O^-		23.4	(+) 37.7	[43]	CH_2F		94.4	(+) 54.8	[53]
CH_2OH		34.5	(+) 45.3	[44]	CHF_2		160.3	(+)148.8	[53]
					CF_3		224.0	(+)271.6	[53]

corresponding values obtained by the UHF INDO methods [2, 5], before and after the annihilation of the quartet spin component. The least square parameters reported in the same table, that is the standard deviation and the correlation coefficient, provide a convenient criterion for comparing the results obtained by the different methods of calculation of the spin density.

The number of experimental points used in the least square procedure to obtain the parameter correlating a_N with $\rho_{s_N s_N}$ is almost equivalent to those used in preceding works [2, 5]. However in the present work a smaller number of radicals,

Table 6. Observed and calculated hfs coupling constants for ^{14}N

		a_N (gauss)					a_N (gauss)		
Radical	Atom	Calcd.	Exptl.	Ref.	Radical	Atom	Calcd.	Exptl.	Ref.
CN		9.5	(+) 4.5	[58]	pyrazine$^-$		8.6	(+) 7.2	[39]
HCN^-		2.9	(+) 7.0	[29]	pyridazine$^-$		9.0	(+) 5.9	[39]
H_2CN		10.3	(+) 9.5	[29]	pyrimidine$^-$		5.0	(+) 3.3	[38]
CH_2CN		6.3	(+) 3.5	[28]	tetrazine$^-$		6.3	(+) 5.3	[39]
CH_3CHCN		5.4	(+) 3.4	[28]	benzonitrile$^-$		2.4	(+) 2.2	[40]
NH_2		15.8	(+) 10.3	[30]	terephthalo-				
NH_3^+		25.6	(+) 19.5	[31]	nitrile$^-$		1.7	(+) 1.8	[40]
$(CH_3)_2N$		18.0	(+) 14.8	[32]	isophthalo-				
$(CH_3)_2NH^+$		19.7	(+) 19.3	[33]	nitrile$^-$		0.6	(+) 1.0	[40]
hydrazine$^+$		13.2	(+) 11.5	[34]	phthalonitrile$^-$		1.4	(+) 1.8	[40]
1-methyl-					NCO		2.6	(+) 11.0	[64]
hydrazine$^+$	1	13.8	(+) 13.2	[35]				(±7.0)	
	2	10.9	(+) 10.4	[35]	NO_2		51.9	(+) 54.7	[65]
1,1-dimethyl-					$NO_2^{-\,-}$		12.0	(+) 14.3	[66]
hydrazine$^+$	1	13.5	(+) 16.1	[36]	$CH_3NO_2^-$		13.3	(+) 25.9	[46]
	2	9.4	(+) 9.7	[36]	nitrobenzene$^-$		11.3	(+) 9.7	[67]
1,2-dimethyl-					*m*-dinitro-				
hydrazine$^+$		11.9	(+) 13.0	[35]	benzene$^-$		1.6	(+) 4.1	[48]
trans					*p*-dinitro-				
1,2-dimethyl-					benzene$^-$		0.8	(+) 1.5	[49]
hydrazine$^+$		11.6	(+) 14.7	[35]	3,5-dinitro-				
cis					pyridine$^-$	–N=	– 1.0	(–) 1.4	[50]
tetramethyl-						NO_2	1.1	(+) 3.8	[50]
hydrazine$^+$		7.6	(+) 13.5	[37]	NF_2		12.1	(+) 16.1	[68]
pyridine$^-$		10.0	(+) 6.3	[38]	2-fluoropyridine$^-$		8.7	(+) 4.8	[56]

Table 7. Observed and calculated hfs coupling constants for ^{17}O

		a_N (gauss)					a_N(gauss)		
Radical	Atom	Calcd.	Exptl.	Ref.	Radical	Atom	Calcd.	Exptl.	Ref.
CH_2OH		9.8	(+) 9.7	[44]	*p*-benzosemi-				
nitrobenzene$^-$		8.8	(+) 8.8	[67]	quinone$^-$		11.7	(+) 9.4	[69]
p-dinitrobenzene$^-$		2.1	(+) 3.8	[49]	FO_2	FO–	11.9	(+) 14.5	[70]
o-benzosemi-						–O	20.4	(+) 22.2	[70]
quinone$^-$		11.7	(+) 8.1	[61]					

Table 8. Observed and calculated hfs coupling constants for ^{19}F

		a_N (gauss)					a_N (gauss)		
Radical	Atom	Calcd.	Exptl.	Ref.	Radical	Atom	Calcd.	Exptl.	Ref.
FO_2		8.8	(+) 12.8	[70]	CH_2CF_3		68.7	(+) 29.8	[54]
NF_2		66.5	(+) 60.3	[68]	CF_2CF_3	CF_2	105.4	(+) 84.9	[72]
FCO		293.0	(+)334.2	[71]		CF_3	2.8	(+) 11.2	[72]
CH_2F		65.0	(+) 64.3	[53]	monofluoro-				
CHF_2		74.4	(+) 84.2	[53]	acetamide		66.2	(+) 54.6	[73]
CF_3		133.4	(+)142.4	[53]	difluoro-				
CH_2CH_2F		94.1	(+) 45.4	[54]	acetamide		74.0	(+) 75.0	[74]
CH_2CHF_2		89.2	(+) 49.5	[55]	2-fluoropyridine$^-$		– 2.2	(–) 7.1	[56]

obtained by parent neutral hydrocarbons of large dimension, have been included into the calculation. On the other hand, small σ and π radicals, built up by different atoms, have been taken into consideration, so that the most important molecular environments, in which the different atoms can be found, have been adequately represented in our sample.

As discussed in a previous work [9] the criteria of choosing the configurations, which have to be included into the CI treatment, is important, as both their type and number affect the calculation of the spin density. From Table 10, where the contributions of the individual types of configurations to the total spin densities of the small radicals are reported, it emerges that for π radicals the contribution of A, B, and C_α configurations is negligible with respect to that of C_β ones. Conversely for σ radicals the contribution of A, B, and C_α configurations can be large, as for example in the case of NO_2 and pyramidal CH_2O^- radicals.

However it must be recognized that this contribution is generally small if compared with the total spin density. Each calculated a_N is modified by less than the corresponding relative deviation, so that the exclusion of A, B, and C_α configurations in the CI treatment does not affect qualitatively the calculated overall spin distribution of the radicals.

With regard to the choice of C_β configurations it has been verified that also the configurations involving the highest energy virtual orbitals give significant contribution to the spin density. As a consequence the C_β configurations must be selected without neglecting the lowest occupied and the highest virtual MO's, by which C_β configurations can be generated. It is important to choose, among all the possible configurations, the most strongly interacting with the ground one. For example the spin distribution of benzyl radical as a function of the number and the type of configurations, is shown in Table 11.

This table shows that a large number of configurations (110 out of 289 possible C_β's) are required to get convergence at spin densities. However 80 configurations are enough to reproduce the spin distribution in a reasonable way.

Table 9. Result of the least square fitting between a_N (gauss) and s-orbital calculated spin densities $\rho_{s_N s_N}$

Nucleus	No. of data points		$(4\pi/3)g\beta\gamma_N\hbar\langle s_z\rangle^{-1}\lvert\phi_{s_N}(r_N)\rvert^2$ (gauss)			$\lvert\phi_{s_N}(r_N)\rvert^2$ (a.u.)$^{-3}$				Standard deviation (gauss)			Correlation coefficient		
			UHF		RHF + CI	UHF		RHF + CI		UHF		RHF + CI	UHF		RHF + CI
	UHF	RHF+CI	*su*[b]	*sa*[c]		*su*	*sa*		SCF[d]	*su*	*sa*		*su*	*sa*	
	[a]														
^1H	141	101	539.86	711.25	612.93	0.338	0.446	0.384	0.317[e]	7.3	6.6	9.2	0.88	0.91	0.95
^{13}C	26	31	820.10	828.97	888.41	2.042	2.065	2.213	2.767	23.8	19.4	28.3	0.93	0.95	0.94
^{14}N	29	37	379.34	1126.8	569.83	3.292	9.777	4.946	4.770	2.3	2.3	3.8	0.76	0.75	0.92
^{17}O	5	7	888.68	2064.4	1967.4	41.08	120.4	90.96	7.638	2.7	2.7	2.4	0.52	0.50	0.92
^{19}F	9	14	44839.0	47884.0	34637.0	29.85	31.87	23.06	11.97	22.2	33.7	24.9	0.92	0.85	0.96

[a] Ref. [5].

[b] Spin unrestricted wavefunction.

[c] Spin annihilated wavefunction.

[d] Ref. [75].

[e] Estimated from the observed a_H for hydrogen atom.

Table 10. Contribution of G, C_β and A, B, C_α configurations to the spin densities of π and σ radicals (RHF + CI method)

Radical	Type	Atom	$\rho_{ss,G}$	ρ_{ss,C_β}	ρ_{ss,A,B,C_α}	ρ_{ss}
CH_3	π	C	0.0	+0.04576	+0.00001	+0.04577
		H	0.0	−0.02835	−0.00001	−0.02836
NH_2		H	0.0	−0.02524	−0.00004	−0.02528
		N	0.0	+0.02773	+0.00038	+0.02811
NCO		C	0.0	−0.00806	−0.00097	−0.00903
		N	0.0	+0.00462	+0.00119	+0.00581
		O	0.0	+0.01465	−0.00122	+0.01343
NO_2^{--}		N	0.0	+0.02105	+0.00011	+0.02116
		O	0.0	+0.00322	−0.00001	+0.00321
NF_2		N	0.0	+0.02124	+0.00017	+0.02141
		F	0.0	+0.00192	+0.00000	+0.00192
FO_1O_2		O_1	0.0	+0.00603	+0.00002	+0.00605
		O_2	0.0	+0.01036	+0.00007	+0.01043
		F	0.0	+0.00025	+0.00000	+0.00025
NH_3^+		H	0.0	−0.03062	−0.00002	−0.03065
		N	0.0	+0.04479	+0.00008	+0.04487
CH_2O^- [a]		H	0.0	−0.01766	−0.00001	−0.01767
		C	0.0	+0.02632	−0.00001	+0.02631
		O	0.0	+0.00798	+0.00001	+0.00799
CN	σ	C	+0.21616	−0.02629	−0.00041	+0.18946
		N	+0.03569	−0.01905	+0.00039	+0.01703
C_1C_2H		H	+0.03274	+0.02353	+0.00503	+0.06130
		C_1	+0.35520	−0.00927	+0.00160	+0.34753
		C_2	+0.02194	−0.00883	−0.00005	+0.01306
HBO^-		H	+0.10315	+0.02002	+0.00776	+0.13093
		B	+0.29207	−0.01037	+0.00248	+0.28418
		O	+0.00172	+0.00252	+0.00031	+0.00456
HCN^-		H	+0.23666	+0.03634	+0.01503	+0.28803
		C	+0.21999	−0.00995	−0.00491	+0.20513
		N	+0.00030	+0.00479	−0.00002	+0.00507
HCO		H	+0.11613	+0.02410	+0.01294	+0.15317
		C	+0.18370	−0.00902	+0.00340	+0.17808
		O	+0.00082	+0.00448	+0.00019	+0.00549
CO_2^-		C	+0.18868	−0.01406	+0.00774	+0.18236
		O	+0.00286	+0.00018	+0.00079	+0.00383
FCO		C	+0.26241	−0.01502	+0.00284	+0.25023
		O	+0.00085	+0.00138	+0.00032	+0.00255
		F	+0.00870	−0.00024	+0.00074	+0.00920
NO_2		N	+0.09956	−0.00867	+0.00906	+0.09995
		O	+0.00063	+0.00112	+0.00051	+0.00226
H_2CN		H	+0.07546	+0.04183	+0.02001	+0.13730
		C	+0.00000	−0.01822	−0.00131	−0.01953
		N	+0.00000	+0.01803	−0.00024	+0.01779
CH_2O^- [b]		H	+0.02912	−0.00218	+0.00593	+0.03287
		C	+0.10901	+0.01082	+0.01059	+0.13042
		O	+0.00022	+0.00664	−0.00001	+0.00685

Table 10—*cont.*

Radical Type	Atom	$\rho_{ss,G}$	ρ_{ss,C_β}	ρ_{ss,A,B,C_α}	ρ_{ss}
CH_2F	H	+0.01432	−0.01879	−0.00146	−0.00593
	C	+0.08442	+0.02183	−0.00233	+0.10392
	F	+0.00061	+0.00127	−0.00001	+0.00187

[a] Planar geometry.
[b] Pyramidal geometry.

The comparison between the results obtained by UHF and RHF + CI methods in the framework of INDO approximation comes both from the overall results and the statistical parameters collected in Table 9. The correlations between calculated and experimental hfs coupling constants for nitrogen, fluorine, and oxygen are statistically more significant when the RHF + CI method is used. In the case of ^1H and ^{13}C the two methods give results which can be considered statistically equivalent (see Table 9).

In the case of ^{17}O it is noteworthy that the term $|\phi_{s_O}(r_O)|^2$ is still largely different from the corresponding value calculated by SCF theory for the free atom [75] even if we get a significant improvement on the correlation coefficient with respect to the UHF one. This result suggests that the INDO wavefunction obtained by employing a minimal basis set gives a poor description of the spin distribution on oxygen atoms, so that an exceedingly high value of $|\phi_{s_O}(r_O)|^2$ is necessary to reproduce the experimental hfs coupling constant.

On the whole it seems that the RHF + CI method leads to hfs coupling constants in better agreement with the experimental values, than the UHF technique. By recalling that the UHF wavefunctions do not represent pure spin states, even after the quartet component annihilation, the conclusion can be drawn that RHF + CI technique should be preferred in the calculation of the spin densities of organic radicals.

Table 11. Influence of the configurations in the spin densities, in benzyl radical

No. and type of of configurations[a]	$\rho_{S_N S_N}$								
	C1	C2	C3	C4	C(CH$_2$)	H$_2$	H$_3$	H$_4$	H(CH$_2$)
C_β (50) A, B, C_α (30)	−0.00366	+0.00452	−0.00118	+0.00449	+0.02883	−0.00212	−0.00004	−0.00250	−0.01617
C_β (50)	−0.00363	+0.00425	−0.00100	+0.00401	+0.03073	−0.00196	−0.00009	−0.00214	−0.01785
C_β (80)	−0.00599	+0.00524	−0.00214	+0.00407	+0.03145	−0.00304	−0.00030	−0.00241	−0.02051
C_β (90)	−0.00608	+0.00531	−0.00214	+0.00426	+0.03145	−0.00364	−0.00010	−0.00296	−0.02059
C_β (100)	−0.00625	+0.00539	−0.00237	+0.00427	+0.03143	−0.00409	−0.00072	−0.00320	−0.02063
C_β (110)	−0.00624	+0.00538	−0.00236	+0.00427	+0.03143	−0.00411	−0.00077	−0.00323	−0.02064

[a] All the MO's have been taken into consideration.

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