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Relationes

Calculations of the Isotropic Hyperfine Coupling Constants in Free Radicals

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For a number of free radicals the results of non-empirical (*ab initio*) and semi-empirical (INDO, DEPAC, CNDO/SP) calculations of the isotropic hyperfine coupling constants are compared.

Key words: Radicals – Spin-density distribution – Hyperfine coupling constants – Electron spin resonance

In the last few years there has been considerable interest in semi-empirical calculations of the hyperfine coupling constants (hfc) in free radicals. Several methods have been suggested for this purpose. Here, for a number of free radicals the calculations of isotropic hfc were carried out by some of these methods using the same values of geometrical parameters. It allows the adequacy of various semi-empirical methods to be analysed on the basis of comparison with the results of experiment as well as available *ab initio* calculations.

(I). *Ab initio* UHF *method* [1–10] followed by annihilation of the contaminating quartet spin state after energy minimization (UHF/AA method [2–7]) was used for most radicals presented in Table 1.

(II). INDO *method* [11] is a semi-empirical SCF LCAO MO one with special selection of the most adequate parameters reproducing the wavefunctions obtained by a more sophisticated calculation of some simple "standard" molecules. By comparison with the results of *ab initio* consideration of more complex molecules it was demonstrated [12–16] that INDO may be a sufficiently effective approach to the problem of calculating the molecular properties. To our knowledge, nothing similar has been done in the case of free radicals.

It is worth mentioning at this point that in the INDO calculations of hfc the spin populations of the AO's are taken to be equal to differences in the α- and β-electron populations

$$\varrho_{\mu\nu} = P^{\alpha}_{\mu\nu} - P^{\beta}_{\mu\nu}, \tag{1}$$

$$P^{\alpha}_{\mu\nu} = \sum_{i}^{\text{occ}} c^{\alpha}_{i\mu} \cdot c^{\alpha}_{i\nu}, \quad P^{\beta}_{\mu\nu} = \sum_{i}^{\text{occ}} c^{\beta}_{i\mu} \cdot c^{\beta}_{i\nu}, \tag{2}$$

where $c^{\alpha}_{i\mu}$, $c^{\beta}_{i\mu}$ are the coefficients of the AO φ_{μ} in the MO's expressions (Ψ^{α}_{i} and Ψ^{β}_{i}) obtained within the scope of the UHF method.

(III). DEPAC *method* is also a semi-empirical SCF LCAO MO scheme [17]. In this method the spin populations are similarly defined with the help of Eqs. (1) and (2). However, as distinct from INDO, the MO's Ψ^{α}_{i} and Ψ^{β}_{i} are

Table 1. Isotropic hyperfine coupling constants (in *G*)

Radical (1)		*ab initio* (2)	INDO (3)	DEPAC (4)	CNDO/SP (5)	Expt. (6)
1. CH_3	H	– 18.0	– 20.6	71.5	– 23.1	(–) 23.0[30]
	C	31.7	43.1	– 72.7	60.4	38.3 [31]
2. $C{\equiv}CH$	H		34.6	106.5	31.6	16.1[32]
	C		287.4	252.6	282.3	—
	C		7.0	– 16.2	7.2	—
3. $HC{=}CH_2$	H	– 1.3	10.7	70.1	13.4	13.4 [30]
($\theta = 135°$)	H	42.8	33.8	87.3	37.9	37.0 [30]
	H	62.4	74.0	113.5	73.6	65.9[30]
	C	139.3	127.7	107.8	125.4	107.6[31]
	C	– 16.4	– 14.9	– 23.4	– 2.4	(–) 8.6 [31]
4. C_6H_5	H		18.7	59.1	17.6	17.4 [33]
	H		6.7	42.8	5.6	5.9 [33]
	H		3.7	40.3	5.5	1.9[33]
	C		149.7	83.2	143.4	
	C		– 3.9	– 8.5	1.2	
	C		9.9	8.0	10.5	
	C		– 1.8	– 5.9	– 1.1	
5. $C{\equiv}N$	C	339.2	149.4	151.6	191.8	210.0 [34]
	N	– 6.2	4.1	12.4	8.6	(–) 4.5 [34]
6. HCN^-	H	140.3	148.9	170.3	147.7	137.5[35]
	C	74.4	156.1	165.8	140.7	74.3 [35]
	N	4.9	3.1	1.5	4.1	6.5 [35]
7. H_2CN	H	84.8	56.1	111.5	63.5	92.1[36]
	C	– 18.7	– 22.6	– 28.0	– 6.6	—
	N	7.2	8.2	2.9	8.5	9.5 [36]
8. HCO	H	112.5	112.7	151.2	115.5	127.0[37]
	C	148.4	146.7	146.6	138.6	131.0 [37]
	O	– 1.0	– 5.2	– 3.2	– 14.2	—
9. CH_3CO	H	4.9	5.4	62.6	3.4	5.1[38]
	C	153.2	128.2	101.8	129.0	125.5[38]
	C	39.9	17.6	6.6	23.6	47.5 [38]
	O	– 9.4	– 5.8	– 1.5	– 15.8	—
10. FCO	F		326.2	262.2	344.8	325.5[39]
	C		199.6	205.2	179.8	288.7 [39]
	O		– 0.7	– 0.8	– 14.9	—
11. CO_2^-	C		170.2	165.0	140.3	166.7 [40]
	O		– 5.5	– 3.9	– 15.7	(–) 32.1 [40]
12. NH_2	H	– 22.3	– 17.3	105.9	– 20.6	(–) 23.9 [41]
	N	8.2	12.9	6.8	14.5	10.3 [41]
13. NH_3^+	H	– 15.8	– 21.2	89.4	– 23.8	(–) 25.9 [42]
	N	14.8	19.2	– 36.7	21.1	19.5 [42]
14. H_2NO	H	– 8.8	12.9	93.6	15.1	11.9 [43]
	N	11.2	10.4	22.0	12.5	11.9 [43]
	O	—	– 10.9	– 11.2	– 28.4	—
15. NO_2	N		31.3	29.3	21.3	54.8 [44]
	O		0.9	1.5	– 12.7	(–) 16.3 [44]

Table 1 (continued)

Radical (1)		*ab initio* (2)	INDO (3)	DEPAC (4)	CNDO/SP (5)	Expt. (6)
16. NH	H	– 56.7	– 30.4	113.8	– 40.6	
	N	11.6	12.9	6.1	16.6	
17. OH	H	– 41.4	– 16.9	148.9	– 22.4	(–) 22.9[45]
	O	(–)34.1	– 13.2	– 14.4	– 38.2	–
18. H_3O	H		150.9	183.0	135.2	[46]
	O		–249.7	–233.5	–398.0	
19. HBO^-	H	91.6	87.7	104.0	74.5	94.0 [47]
	B	123.0	212.2	223.2	191.9	101.0 [47]
	O	– 4.1	– 4.2	– 1.0	– 8.6	—
20. BH_3^-	H	– 17.2	– 16.9	42.3	– 19.4	(–) 16.5 [47]
	B	13.6	34.6	– 42.1	44.1	25.0 [47]
21. BF_2	B		336.5	355.3	288.2	295.0 [48]
	F		359.4	403.5	181.1	190.0 [48]

accepted as being those of the anion and cation with closed shells formed by "addition" or "subtraction" of one electron from the open electron shell of the corresponding free radical, i.e. the spin populations of the radical AO's are compared to semi-differences in the electron populations of the anion and cation (DEPAC).

With the use of this method the proton hfc in benzyl, allyl and some other conjugated radicals have been calculated within the framework of π-electron approach [17, 18]. For the former the para/ortho ratio greater than unity was readily reproduced with its standard geometry while a more refined consideration proved to be necessary in the usual open-shell methods (cf. INDO [18–20]). Another example is the HCO σ-radical for which the all-valence-electron DEPAC method led to a satisfactory quantitative description of the carbon and hydrogen isotropic constants as well as principal components of the anisotropic hyperfine interaction [21].

Nevertheless it seems to be desirable to carry out systematic calculations of various free radicals by the DEPAC method in order to feel sure that this approach is either effective or unfit. DEPAC values of the isotropic hyperfine coupling constants are summarized in Table 1. They were obtained from consideration of the corresponding anions and cations within the scope of INDO, i.e. with the use of exactly the same approximations for the matrix elements of the Hartree-Fock operator as in the preceding section.

(IV). CNDO/SP *method* [22] may be considered as the consistent extension of the Mc Lachlan procedure to the case of all-valence-electron calculations of the spin density distributions in free radicals. This method is based on the use of the effective hamiltonian for the open-shell electronic states [23] as well as the CNDO/2 approximations [24] within the framework of the restricted Hartree-Fock (RHF) approach.

Table 2. CNDO/SP delocalization and polarization contributions (in *G*)

Radical (1)		a^0 (2)	a^{sp} (3)	a^{ep} (4)
1. CH_3	H	0	0	-23.1
	C	0	0	-60.4
2. $C{\equiv}CH$	H	36.3	- 0.6	- 4.1
	C	272.8	- 1.9	11.4
	C	21.3	- 5.7	- 8.4
3. $HC{=}CH_2$	H	29.7	- 5.2	-11.1
	H	39.7	0.9	- 2.7
	H	75.4	1.7	- 3.5
	C	91.9	- 3.3	36.8
	C	4.1	- 1.9	- 4.6
4. C_6H_5	H	20.0	0.2	- 2.6
	H	7.5	- 0.3	- 1.6
	H	5.6	0.1	- 0.2
	C	117.6	- 4.4	30.2
	C	5.1	- 1.4	- 2.5
	C	9.5	- 0.4	1.4
	C	0.1	- 0.2	- 1.0
5. $C{\equiv}N$	C	185.3	- 2.3	8.8
	N	6.8	- 1.1	2.9
6. HCN^-	H	153.1	1.1	- 6.5
	C	140.5	0.4	- 0.2
	N	0.1	- 0.2	4.2
7. H_2CN	H	64.7	- 1.0	- 0.2
	C	0	- 1.6	- 5.0
	N	0	0	8.5
8. HCO	H	125.6	- 0.9	- 9.2
	C	131.8	- 0.8	7.6
	O	-0.4	0.5	-14.3
9. CH_3CO	H	7.2	- 0.1	- 3.7
	C	117.7	- 1.4	12.7
	C	21.5	- 0.7	2.8
	O	-0.3	2.6	-18.1
10. FCO	F	284.3	-31.3	91.8
	C	174.7	0.4	4.7
	O	-0.6	1.2	-15.5
11. CO_2^-	C	127.5	- 2.6	15.4
	O	-6.3	1.3	-10.7
12. NH_2	H	0	0	-20.6
	N	0	0	14.5
13. NH_3^+	H	0	0	-23.8
	N	0	0	21.1
14. H_2NO	H	20.6	- 0.6	- 4.9
	N	11.3	- 0.4	1.6
	O	-0.3	2.2	-30.3
15. NO_2	N	17.2	- 0.6	4.7
	O	-0.4	1.0	-13.3

Table 2 (Continued)

Radical (1)		a^0 (2)	a^{sp} (3)	a^{ep} (4)
16. NH	H	0	0	−40.6
	N	0	0	16.6
17. OH	H	0	0	−22.4
	O	0	0	−38.2
18. H_3O	H	146.8	2.9	−14.5
	O	−398.0	0	0
19. HBO^-	H	86.3	− 0.8	−11.0
	B	187.8	0.8	3.3
	O	−0.8	1.0	− 8.8
20. BH_3^-	H	0	0	−19.4
	B	0	0	44.1
21. BF_2	B	288.4	0.5	− 0.7
	F	234.3	−21.5	−31.7

According to CNDO/SP the spin density matrix may be presented as a sum of three constituents namely

1) the one electron (delocalization) term $\hat{\varrho}^0$
2) the spin-polarization term $\hat{\varrho}^{sp}$ and
3) the exchange $(\sigma - \pi)$ spin-polarization term $\hat{\varrho}^{ep}$.

The delocalization contribution $\varrho^0_{\mu\mu}$ to the spin population of the AO φ_μ is accepted as being the square of the coefficient by this AO in the unpaired electron MO expression. The other two contributions to the spin population, arising from the unpaired electron polarization of paired electrons in doubly occupied MO's are calculated by a perturbation theory with the help of "atom-atom" mutual polarizabilities $(\pi_{\mu\nu})$ of Coulson [25] and the values of the atomic electron repulsion $(\gamma_{\mu\nu})$ and exchange $(\varkappa_{\sigma\nu})$ integrals

$$\varrho^{sp}_{\mu\mu} = -\tfrac{1}{2} \cdot \lambda_{sp} \cdot \sum_\nu \pi_{\mu\nu} \cdot \gamma_{\nu\nu} \cdot \varrho^0_{\nu\nu}\,, \tag{3}$$

$$\varrho^{ep}_{\mu\mu} = -\tfrac{1}{2} \cdot \lambda_{ep} \cdot \sum_\nu \pi_{\mu\nu} \cdot \sum_\sigma \varkappa_{\sigma\nu} \cdot (\varrho^0_{\sigma\sigma} + \varrho^{sp}_{\sigma\sigma})\,. \tag{4}$$

Here, as in the Mc Lachlan method, the semi-empirical parameters are introduced whose magnitudes $\lambda_{sp} = 0.1$ and $\lambda_{ep} = 2.35$ have been found from comparison with experiment.

The contributions to isotropic hfc are summarized in Table 2. CNDO/SP calculations of hfc were carried out with the semi-empirical quantities

$$\delta_N = \tfrac{4}{3} \cdot \pi \cdot g_e \cdot \beta_e \cdot \gamma_N \cdot \hbar \cdot \langle S_Z \rangle^{-1} \cdot |S(0)|^2 \tag{5}$$

presented in Table 3 together with those obtained [26] by least-squares fitting for INDO. The Hartree-Fock values [27] are also given in this table for comparison.

INDO as well as DEPAC and CNDO/SP calculations were performed for the same geometrical structure of any free radical in Table 1. In most cases the

Table 3. δ_N-parameters for magnetic nuclei (in G)

Nucleus	HF	INDO	CNDO/SP
^{1}H	508	539.86	600
^{11}B	725	(725)	700
^{13}C	1130	820.10	850
^{14}N	552	379.34	300
^{17}O	− 1660	− 888.68	− 1500
^{19}F	17200	44829.20	36500

values of bond lengths and angles were estimated as those recommended for molecules [28] or taken from experiment if possible. Note that in *ab initio* calculations [1–10] the radical geometry was either similar or it was varied.

The results, summarized in Table 1, suggest the following conclusions:

1. Most of the experimental trends for the isotropic hfc in free radicals are well reproduced by the INDO method. The difference between the *ab initio* and INDO results is small as a rule in spite of the proper variation of parameters in *ab initio* calculations [2–7, 9]. This may partly justify some applications of the INDO method for semi-quantitative hfc predictions. On the other hand, INDO is rather simple and more economical and therefore practically preferable in the case of complex paramagnetic species. At present it can be considered as the best among the semi-empirical methods for hfc calculations [26].

2. As distinct from INDO, the DEPAC method is generally unable to reproduce the experimental hfc data reliablely. Moreover DEPAC leads to unreasonable qualitative results when a^{ep} is the only contribution to the isotropic hfc (cf. Table 2). Thus DEPAC is unfit for the all-valence-electron calculations of π-electron free radicals. However, it is of interest to note that for some σ-electron radicals ($C{\equiv}N$, HCN^-, H_2CN, HCO, CO_2^-, NO_2, H_3O, HBO^-) there is a good qualitative accordance between the hfc magnitudes obtained by DEPAC and INDO. Nevertheless, for the σ-electron radicals such as $C{\equiv}CH$, $HC{=}CH_2$, C_6H_5, CH_3CO the DEPAC method again proves to be unsatisfactory.

3. CNDO/SP method is the most economical and simple among those presented in Table 1. At the same time the results indicate that CNDO/SP is sufficiently effective as it leads to a satisfactory quantitative description of hfc. As distinct from INDO, the CNDO/SP approach facilitates the qualitative interpretation of the experimental data substantially as it allows the spin density matrix to be presented as a sum of the one electron and spin-polarization constituents and also makes possible the direct comparison with the results of simpler methods [29]. This approach is very attractive for the practical calculations due to the opportunity of estimating the one electron contribution reliablely and obtaining a small spin-polarization correction by a perturbation theory.

Rather large values of the exchange spin-polarization terms a^{ep} for σ-electron radicals are worth mentioning at this point. They may be compared with similar INDO-magnitudes a^{ep} which are the UHF-differences in the isotropic hyperfine

Table 4. Isotropic hyperfine coupling constants and exchange spin-polarization contributions (in *G*)

Method		INDO	CNDO/2	INDO	CNDO/SP
hfc		*a*	*a*	a^{ep}	a^{ep}
$HC{=}CH_2$	H	10.7	29.2	-18.5	-11.1
	H	33.8	37.3	-3.5	-2.7
	H	74.0	73.4	0.6	-3.5
	C	127.7	91.0	36.7	36.8
	C	-14.9	-9.1	-5.8	-4.6
$C{\equiv}CH$	H	34.6	30.3	4.3	-4.1
	C	7.0	9.4	-2.4	-8.4
	C	287.4	274.0	13.4	11.4
HCN^-	H	148.9	155.0	-6.1	-6.5
	C	156.1	126.8	29.3	-0.2
	N	3.1	-0.3	3.4	4.2
HCO	H	112.7	128.0	-15.3	-9.2
	C	146.7	108.7	38.0	7.6
	O	-5.2	0.4	-5.6	-14.3
HBO^-	H	87.7	92.1	-4.4	-11.0
	B	212.2	181.0	31.2	3.3
	O	-4.2	0.2	-4.4	-8.8

coupling constants calculated within the scope of INDO and CNDO/2, as the latter neglectes the atomic exchange integrals $\varkappa_{\sigma\nu}$. These differences for some σ-electron radicals are summarized in the last but one column of Table 4. In most cases they are much the same or greater than those obtained by the CNDO/SP method.

A good quantitative agreement with the experimental and INDO results shows a strong evidence for the efficiency of CNDO/SP in qualitative analyses of the isotropic hfc.

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