

Calculation of Spin Densities in Odd Alternant Hydrocarbon Radicals

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Spin densities in benzyl, allyl, pentadienyl and perinaphthenyl radicals have been calculated with some variants of the simplified McLachlan unrestricted SCF method based on Hückel-type and the SC Hückel-type molecular orbitals. The various estimations of the spin densities were compared one with each other and with the results of more sophisticated methods. It was shown that the SC Hückel basis and Zhidomirov and Schastnev's modification of the McLachlan approach give a best least square fit of the relation $a_{\mu}^{\text{exp}} \approx Q_{\mu}^{\text{calc}}$.

Die Spindichten von Benzyl-, Allyl-, Pentadienyl- und Naphtenyl-Radikalen werden mit einigen Varianten der uneingeschränkten SCF-Methode in der vereinfachten Form nach McLachlan, die auf den Hückel- und den SC-Hückel-Molekülorbitalen basiert, berechnet. Die verschiedenen Schätzungen der Spindichten werden miteinander sowie mit den Resultaten komplizierterer Methoden verglichen. Es wird gezeigt, daß die SC Hückel Basis und die von Zhidomirov und Schastnev eingeführte Modifikation der Näherung von McLachlan eine beste Näherung nach der Methode der kleinsten Quadrate an die Beziehung $a_{\mu}^{\text{exp}} \approx Q_{\mu}^{\text{calc}}$ ergeben.

Les densités de spin ont été calculées dans les radicaux benzyle, allyle, pentadiényle et perinaphthényle à l'aide de variantes de la méthode SCF sans restrictions de spin simplifiée de Mac Lachlan, en utilisant des orbitales de type Hückel et SC Hückel. Les différentes évaluations de densité de spin sont comparées entre elles et avec celles obtenues par des méthodes plus élaborées. On montre que la base SC Hückel et la modification de Zhidomirov et Schastnev à la théorie de Mac Lachlan donnent le meilleur accord au sens des moindres carrés avec la relation $a_{\mu}^{\text{exp}} \approx Q_{\mu}^{\text{calc}}$.

The selfconsistent modification of the simple Hückel method (SCH method) [1] is known to be successful in explanation of several physical and chemical properties of conjugated hydrocarbons and some heterocyclic molecules [1–10]. It is known that the results of this method are much more adequate than those which follow from the standard Hückel approach. It is thus interesting to compare the applicability of these two methods for a calculation of spin densities within the McLachlan framework.

We recall that in the SCH method the resonance integral for next neighbours, $\beta_{\mu\nu}$, depends exponentially on the bond length $R_{\mu\nu}$,

$$\beta_{\mu\nu} = \beta_{\mu\nu}^0 \exp[-g(R_{\mu\nu} - 1.397)] \quad (1)$$

where

$$R_{\mu\nu} = a - b p_{\mu\nu}, \quad (2)$$

g, a, b are constants, and $p_{\mu\nu}$ is the mobile bond order between atoms μ and ν . In the case of hydrocarbons we take $\beta_{\mu\nu}^0 = \beta^0 = \text{const.}$, $g = 4$, $a = 1.517$ and $b = 0.180$. The calculations are carried out until selfconsistency of Eqs. (1) and (2) is obtained.

Zhidomirov and Schastnev [11] calculated the spin densities in benzyl and cyclohexadienyl radicals recently with a modified McLachlan method, based on SCH-type MO's. They have obtained a remarkable agreement with experiment.

The purpose of the present work is:

1. to extend their discussion to other conjugated neutral hydrocarbon radicals,
2. to give a derivation of Zhidomirov and Schastnev's modification of the McLachlan approach,
3. to investigate the rôle of the choice of the basis (SCH MO's or H MO's),
4. to discuss other possible modifications of the McLachlan approach,
5. to test the various sets of calculated spin densities by a least square fit to the McConnell relationship,
6. to compare these results with those obtained with more sophisticated methods.

The Original and Modified McLachlan Methods

As well known the McLachlan method [12] is a perturbation treatment of the UHF method [13, 14]. According to Bristock and Pople [14] the UHF LCAO molecular spinorbitals¹

$$\Psi_j^{\alpha(\beta)} = \sum_{\mu} c_{j\mu}^{\alpha(\beta)} \varphi_{j\mu}^{\alpha(\beta)} \quad (3)$$

are calculated from Eq. (4)

$$\sum_{\nu} F_{\mu\nu}^{\alpha(\beta)} c_{j\nu}^{\alpha(\beta)} = E_j^{\alpha(\beta)} c_{j\mu}^{\alpha(\beta)}, \quad (4)$$

where (using the standard notation [15, 16]),

$$F_{\mu\mu}^{\alpha(\beta)} = -I_{\mu} + P_{\mu\mu}^{\beta(\alpha)} \gamma_{\mu\mu} + \sum_{\sigma \neq \mu} (P_{\sigma\sigma} - 1) \gamma_{\mu\sigma}, \quad \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \quad (5)$$

$$F_{\mu\nu}^{\alpha(\beta)} \left\{ \begin{array}{ll} = \beta_{\mu\nu}^c - P_{\mu\nu}^{\alpha(\beta)} \gamma_{\mu\nu} & \text{for neighbours,} \\ = -P_{\mu\nu}^{\alpha(\beta)} \gamma_{\mu\nu} & \text{for non-neighbours.} \end{array} \right.$$

$$P_{\mu\nu}^{\alpha(\beta)} = \sum_j^{\text{occ}} c_{j\mu}^{\alpha(\beta)} c_{j\nu}^{\alpha(\beta)}, \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \quad (6)$$

$$P_{\mu\nu} = P_{\mu\nu}^{\alpha} + P_{\mu\nu}^{\beta}.$$

The spin density ρ_{μ} for the carbon atom μ is then given by Eq. (7):

$$\rho_{\mu} = P_{\mu\nu}^{\alpha} - P_{\mu\nu}^{\beta}. \quad (7)$$

According to McLachlan the odd electron state affects the closed shell states being not changed itself. The spin densities are calculated then perturbationally,

$$\rho_{\mu} = c_{0\mu}^2 - \frac{1}{2} \sum_{\nu} \pi_{\mu\nu} (F_{\nu\nu}^{\alpha} - F_{\nu\nu}^{\beta}) = c_{0\mu}^2 + \frac{1}{2} \gamma \sum_{\nu} \pi_{\mu\nu} c_{0\nu}^2 \quad (8)$$

¹ Let us recall that the UHF single determinantal wave function is not an eigenfunction of \hat{S}^2 , requiring thus a projection technique for calculation of the pure spin state [17-19].

where $c_{0\mu}$ is the appropriate SCF LCAO coefficient for the unperturbed molecular orbital of the odd electron, $\pi_{\mu\nu}$ is the atom-atom polarizability [20] and $\gamma = \gamma_{\mu\mu} = \text{const}$. In the case of alternant hydrocarbons perturbations of the type

$$F_{\mu\nu}^{\alpha} - F_{\mu\nu}^{\beta} = -c_{0\mu}c_{0\nu}\gamma_{\mu\nu}$$

do not affect the spin density, because $\pi_{\mu,\nu\sigma} = 0$ [21].

However, H-type and SCF-type MO's do not differ significantly. Thus, according to McLachlan²

$$Q_{\mu} = c_{0\mu}^2 + \lambda \sum_{\nu} \pi_{\mu\nu} c_{0\nu}^2 \quad (9)$$

where the Hückel-type MO's can be applied instead, and $\lambda \sim 1.0 - 1.2$ ³.

From the viewpoint of the Hückel method formula (9) is a first order perturbation which follows from Eqs. (10) and (11)

$$Q_{\mu} = c_{0\mu}^2 + \sum_j^{\text{doubly occ.}} [c_{j\mu}^2(2\lambda) - c_{j\mu}^2] \quad (10)$$

where $c_{j\mu}(2\lambda)$'s are the LCAO coefficients which follow from the perturbed Hückel-type energy matrix

$$H_{\mu\nu}(2\lambda) = H_{\mu\nu} + 2\lambda c_{0\mu}^2 \delta_{\mu\nu} \beta^0. \quad (11)$$

Eqs. (9) and (10) were both suggested by McLachlan but only the first one was used by him in practice [12].

The odd electron was assumed here to occupy the unperturbed molecular orbital. However, with analogy to the UHF treatment of odd alternant hydrocarbon radicals, also a different approach is possible. Let us rewrite formula (5) for the diagonal element as follows

$$F_{\mu\mu}^{\alpha} = - \left(I_{\mu} + \sum_{\sigma}' \gamma_{\mu\sigma} \right) + \sum_{\sigma} P_{\sigma\sigma} \gamma_{\mu\sigma} - P_{\mu\mu}^{\alpha} \gamma_{\mu\mu}, \quad (12)$$

$$F_{\mu\mu}^{\beta} = - \left(I_{\mu} + \sum_{\sigma}' \gamma_{\mu\sigma} \right) + \sum_{\sigma} P_{\sigma\sigma} \gamma_{\mu\sigma} - P_{\mu\mu}^{\beta} \gamma_{\mu\mu}. \quad (13)$$

Comparing formulae (12) and (13) with those known from the effective Hamiltonian method of the RHF approach (Longuet-Higgins and Pople [23])

$$F_{\mu\mu}^{\alpha}(0) = F_{\mu\mu}^{\beta}(0) = - \left(I_{\mu} + \sum_{\sigma}' \gamma_{\mu\sigma} \right) + \sum_{\sigma} P_{\sigma\sigma} \gamma_{\mu\sigma} - \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} \quad (14)$$

we note that, applying the eigenvectors of the Longuet-Higgins and Pople method as the zeroth approximation of the UHF method,

$$\Delta F_{\mu\mu}^{\alpha} = F_{\mu\mu}^{\alpha} - F_{\mu\mu}^{\alpha}(0) = -\frac{1}{2} c_{0\mu}^2 \gamma_{\mu\mu}, \quad (15)$$

$$\Delta F_{\mu\mu}^{\beta} = F_{\mu\mu}^{\beta} - F_{\mu\mu}^{\beta}(0) = \frac{1}{2} c_{0\mu}^2 \gamma_{\mu\mu}. \quad (16)$$

² With Heilbronner's definition of $\pi_{\mu\nu}$ [22].

³ From comparison of the elements of the energy matrices in the SCF and simple Hückel methods.

Thus neglecting the correction terms for off-diagonal elements $\Delta F_{\mu\nu}^{\alpha(\beta)}$ (for $\mu \neq \nu$) we obtain the formula used by Zhidomirov and Schastnev [11]

$$Q_{\mu} = c_{0\mu}^2(\lambda) + \sum_j^{\text{doubly occ.}} [c_{j\mu}^2(\lambda) - c_{j\mu}^2(-\lambda)]. \quad (17)$$

Starting with restricted MO's of the closed shell of the cation, on the other hand, we obtain the following perturbation

$$\Delta F_{\mu\mu}^{\alpha} = F_{\mu\mu}^{\alpha} - F_{\mu\mu}^{\alpha}(0) = \sum_{\sigma} c_{0\sigma}^2 \gamma_{\mu\sigma} - c_{0\mu}^2 \gamma_{\mu\mu}, \quad (18)$$

$$\Delta F_{\mu\mu}^{\beta} = F_{\mu\mu}^{\beta} - F_{\mu\mu}^{\beta}(0) = \sum_{\sigma} c_{0\sigma}^2 \gamma_{\mu\sigma}. \quad (19)$$

Replacing now the sum $\sum_{\sigma} c_{0\sigma}^2 \gamma_{\mu\sigma}$ by its average value we obtain $\Delta F_{\mu\mu}^{\alpha} = \text{const} - c_{0\mu}^2 \gamma_{\mu\mu}$ and $\Delta F_{\mu\mu}^{\beta} = \text{const}$. Neglecting thus again the off-diagonal perturbation terms $\Delta F_{\mu\nu}^{\alpha}$ and $\Delta F_{\mu\nu}^{\beta}$ (for $\mu \neq \nu$) and passing back to the Hückel framework we can put

$$Q_{\mu} = c_{0\mu}^2(2\lambda) + \sum_j^{\text{doubly occ.}} [c_{j\mu}^2(2\lambda) - c_{j\mu}^2]. \quad (20)$$

Formula (20) resembles that given by McLachlan, except for the contribution from the odd electron.

In next sections we test the utility of formulae (9), (10), (17) and (20), both for the H-type and SCH-type bases⁴. With this purpose in mind we discuss the correlation between the experimental isotropic hyperfine coupling constant of the proton (a_{μ}) and the calculated π -electronic spin density (Q_{μ}) on the adjacent carbon atom [24]

$$a_{\mu}^{\text{exp}} \approx a_{\mu}^{\text{calc}} = Q_{\mu}. \quad (21)$$

We also compare our results with those obtained by other authors with more sophisticated methods.

Experimental Data

Benzyl Radical. The measurement of hyperfine coupling constants for this radical was carried out by several authors [25–27]. We prefer the results obtained by Carrington, Smith [26] and Fisher [27], owing to the highest accuracy. Dixon and Norman's data [25] are based on a not fully resolved spectrum. Therefore we consider in what follows the mean value of the quoted two data sets only [26, 27].

Allyl and Pentadienyl Radicals. In the case of the allyl radical we consider the data found by Fressenden and Schuler [28] and confirmed later by Kochi and Krusic [41]. To be explicit, we take the average of the two slightly different experimental values for the two outermost positions. As regards the pentadienyl radical no hyperfine coupling constants have been published as yet. In the present work we take the values known for the cyclohexadienyl radical [28] instead. This assumption seems to be quite realistic and it was taken also by other authors [19, 35–40].

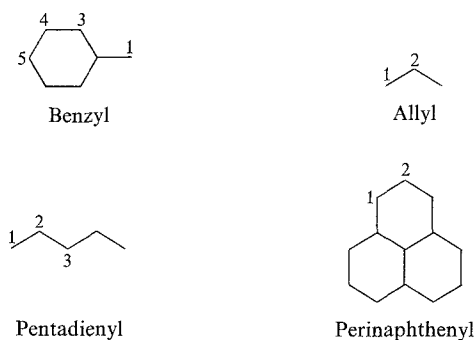


Fig. 1. Numbering of positions

Table 1. *Experimental hyperfine coupling constants*^a

Radical	μ^b $ a_\mu^{\text{exp}} $ from the various sources ^c			Accepted as $ a_\mu^{\text{exp}} $ in the present paper	
	1	2	3		
Benzyl	1	16.4 (± 0.3) [25]	16.35 (± 0.05) [26]	16.40 (± 0.10) [27]	16.38
	3	5.1	5.14	5.17	5.16
	4	1.6	1.75	1.77	1.76
	5	6.3	6.14	6.19	6.16
Allyl	1	14.38 (± 0.02) [28, 41]			14.38
	2	4.06			4.06
Pentadienyl	1	8.99 (± 0.02) [28]			8.99
	2	2.65			2.65
	3	13.04			13.04
Perinaphthenyl	1	6.29 (± 0.04) [29]	6.3 (± 0.1) [31, 32]		6.29
	2	1.81 (± 0.02)	1.82 (± 0.05)		1.81

^a In gauss.^b Numbering of positions is given in Fig. 1.^c Experimental standard error is given in brackets.

Perinaphthenyl Radical. We discuss Gerson's data [29] because of their higher accuracy than of the older ones obtained by Sogo, Nakazaki, and Calvin [30]. Besides, Gerson's data are very close to those obtained by Bennett [31, 32]. All these experimental data are listed in Column 4 of Table 1.

Discussion

Discussing the correlation between the calculated spin densities and the experimental hyperfine coupling constants one must know λ . In the original McLachlan treatment he assumed the value $\lambda = 1.00$ for the benzyl radical, 1.06 for the allyl radical and 1.15 for the perinaphthenyl one [12]. In a preliminary analysis we found that a common value $\lambda = 1$ is sufficiently accurate provided the McConnell relation (21) is used.

Table 2. Spin densities (q_μ) calculated from formulae (9), (10), (17), and (20) for $\lambda = 1$

Radical	μ^a	H MO's				SCH MO's		
		Eq. (9)	Eq. (10)	Eq. (17)	Eq. (20)	Eq. (10)	Eq. (17)	Eq. (20)
1	2	3	4	5	6	7	8	9
Benzyl	1	0.770	0.890	0.722	0.690	0.715	0.621	0.597
	3	0.161	0.156	0.167	0.172	0.191	0.200	0.203
	4	-0.063	-0.070	-0.061	-0.060	-0.074	-0.072	-0.071
	5	0.137	0.086	0.153	0.163	0.186	0.226	0.234
Allyl	1	0.588	0.583	0.587	0.583	0.583	0.587	0.583
	2	-0.177	-0.167	-0.174	-0.167	-0.167	-0.174	-0.167
Pentadienyl	1	0.433	0.428	0.432	0.428	0.330	0.344	0.346
	2	-0.132	-0.126	-0.130	-0.126	-0.116	-0.114	-0.111
	3	0.398	0.396	0.397	0.396	0.572	0.539	0.530
Perinaphthenyl	1	0.219	0.218	0.219	0.218	0.220	0.221	0.220
	2	-0.060	-0.060	-0.060	-0.060	-0.060	-0.060	-0.060

^a Numbering of positions is given in Fig. 1.

Table 3. Statistical analysis of spin densities (presented in Table 2) with the use of McConnell's relation

Molecular orbitals	Eq.	$-Q$ in gauss ^a	Standard error ^b	Relative error, σ_r ^c	Maximum deviation ^d	Correlation, R ^e
H	(9)	24.06 (1.45)	1.74	0.19	3.46	0.888
	(10)	22.41 (1.85)	2.35	0.22	4.23	0.795
	(17)	24.77 (1.31)	1.53	0.17	3.20	0.912
	(20)	25.32 (1.23)	1.40	0.15	3.01	0.927
SCH	(10)	24.21 (0.68)	0.82	0.10	1.65	0.975
	(17)	25.38 (0.40)	0.46	0.07	0.69	0.992
	(20)	25.78 (0.43)	0.49	0.06	0.99	0.991

^a Standard error of Q is given in brackets.

^b Usual definition [33, 34].

^c Calculated according to the formula: $\sigma_r = \frac{1}{n} \sum_{\mu=1}^n \frac{|a_\mu^{\text{calc}} - a_\mu^{\text{exp}}|}{|a_\mu^{\text{exp}}|}$.

^d Equal to the maximum of $|a_\mu^{\text{calc}} - a_\mu^{\text{exp}}|$.

^e Calculated according to the formula: $R = 1 - \frac{\sum_{\mu=1}^n [(a_\mu^{\text{exp}})^2 - a_\mu^{\text{exp}} \cdot a_\mu^{\text{calc}}]}{\sum_{\mu=1}^n [(a_\mu^{\text{exp}})^2 - \left(\frac{1}{n} \sum_{\mu=1}^n a_\mu^{\text{exp}}\right)^2]}$.

The spin densities which have been obtained from H MO's and SCH MO's, and formulae (9), (10), (17) and (20) are compiled in Table 2⁴.

We see what follows:

1. the spin densities in the allyl and perinaphthenyl radicals are insensitive to the choice of the MO basis and of one of the formulae (10), (17), and (20),

2. in contrast, the spin densities in pentadienyl, and particularly in the benzyl radical, depend strongly on the choice of the MO basis and of one of the formulae (10), (17), and (20),

⁴ Except for the combination: formula (9) and the SCH MO basis.

Table 4. Hyperfine coupling constants^a calculated from the McConnell relationship using the spin densities presented in Table 2 and the values of Q given in Table 3

Radical	μ	$ a_{\mu}^{\text{exp}} ^b$	H MO's				SCH MO's		
			Eq. (9)	Eq. (10)	Eq. (17)	Eq. (20)	Eq. (10)	Eq. (17)	Eq. (20)
Benzyl	1	16.38	-18.53	-19.93	-17.89	-17.47	-17.31	-15.76	-15.39
	3	5.16	-3.87	-3.49	-4.13	-4.35	-4.61	-5.07	-5.24
	4	1.76	1.52	1.56	1.51	1.51	1.80	1.83	1.83
	5	6.16	-3.30	-1.93	-3.78	-4.12	-4.51	-5.74	-6.03
Allyl	1	14.38	-14.15	-13.07	-14.54	-14.77	-14.12	-14.90	-15.04
	2	4.06	4.26	3.74	4.31	4.22	4.04	4.42	4.31
Pentadienyl	1	8.99	-10.42	-9.59	-10.69	-10.84	-7.98	-8.74	-8.92
	2	2.65	3.18	2.83	3.22	3.20	2.80	2.90	2.86
	3	13.04	-9.58	-8.88	-9.84	-10.03	-13.84	-13.69	-13.66
Perinaphthenyl	1	6.29	-5.27	-4.89	-5.41	-5.52	-5.33	-5.60	-5.67
	2	1.81	1.44	1.34	1.49	1.52	1.44	1.52	1.55

^a In gauss.^b As given in last column of Table 1 (see text).

Table 5. Statistical characteristics of the correlation between the experimental hyperfine coupling constants and spin densities calculated with various methods

Source of spin density data	$-Q$ in gauss ^a	Standard error ^b	Relative error ^c	Max. deviation ^d	Correlation ^e
McLachlan ^f	24.06 (1.45)	1.74	0.19	3.46	0.888
This work ^g	25.32 (1.23)	1.40	0.15	3.01	0.927
This work ^h	25.38 (0.40)	0.46	0.07	0.69	0.992
Adam and Laidlaw ⁱ	24.01 (0.59)	0.70	0.14	1.32	0.983
Amos and Snyder ^j	25.85 (1.35)	1.52	0.18	2.85	0.914
Hinchliffe ^k	25.11 (1.00)	1.16	0.14	2.42	0.950
Hinchliffe ^l	23.91 (1.58)	1.90	0.27	4.10	0.865
Amos and Davison ^m	27.53 (1.26)	1.33	0.11	2.96	0.934

^{a-e} See footnotes a-e in Table 3.^f Ref. [12], but for the allyl, pentadienyl and perinaphthenyl radicals calculated from Eq. (9) for $\lambda = 1$.^g H method and formula (20), this paper.^h SCH method and formula (17), this paper.ⁱ SCF method, in which MO's for electrons of α and β spins have been found from the solution of the SCF problem for a molecule having one electron added or removed from the radical, respectively [35].^j UHF AA method [19].^k CI method with the H MO basis [36].^l SCF CI method with the SCF MO basis [37].^m UHF method with the AMO basis [38].

3. McLachlan's formulae (9) and (10) lead in some cases to very different results.

Comparison with experiment with the use of the McConnell relation is presented in Tables 3 and 4. One notes that:

1. the SCH MO basis gives a definitely better agreement with experiment than the H MO one,

Table 6. Hyperfine coupling constants calculated by various methods

Radical	μ^a	$ \alpha_\mu^{\text{exp}} $ in gauss	McL ^b	SH ^c	SCH ^d	SCF ^e	UHF AA ^f	SCF CI ^g	SCF CI ^h	AMO ⁱ	INDO ^j	SE SCF ^k
Benzyl	1	16.38	-18.53	-17.47	-15.76	-17.05	-18.56	-17.80	-19.22	-16.19	-17.0	-14.28
	3	5.16	-3.87	-4.35	-5.07	-3.84	-4.06	-4.42	-2.99	-5.53	-6.4	-6.61
	4	1.76	1.52	1.51	1.83	0.96	1.29	1.51	0.77	1.93	3.6	3.39
Allyl	5	6.16	-3.30	-4.12	-5.74	-5.76	-3.31	-3.74	-2.06	-5.81	-5.6	-6.17
	1	14.38	-14.15	-14.77	-14.90	-14.17	-14.14	-14.97	-13.44	-15.06	-14.8	-13.84
Pentadienyl	2	4.06	4.26	4.22	4.42	4.56	2.40	3.49	2.94	2.59	6.9	3.96
	1	8.99	-10.42	-10.84	-8.74	-8.88	-9.90	-9.54	-7.89	-11.42	-11.1	-10.72
Perinaphthyl	2	2.65	3.18	3.20	2.90	3.36	2.43	2.64	2.20	2.70	5.1	3.78
	3	13.04	-9.58	-10.03	-13.69	-12.73	-10.91	-11.30	-12.50	-10.08	-9.8	-9.84
	1	6.29	-5.27	-5.52	-5.60	-	-5.66	-5.50	-5.14	-6.03	-7.5	-
	2	1.81	1.44	1.52	1.52	-	1.65	1.23	1.27	1.76	4.3	-

^a Numbering of positions is given in Fig. 1.

^b Ref. [12], but for allyl, pentadienyl and perinaphthyl radicals calculated from formula (9) for $\lambda = 1$.

^c H.M.O.'s and formula (20), this paper.

^d SCH MO's and formula (17), this paper.

^e Ref. [35].

^f Ref. [19].

^g Ref. [36].

^h Ref. [37].

ⁱ Ref. [38].

^j Ref. [39], spin densities have been not given.

^k Ref. [40], spin densities have been not given.

2. in both cases formulae (17) and (20) yield definitely better results than the McLachlan formulae (9) and (10),

3. a best agreement with experiment is obtained with the Zhidomirov and Schastnev formula (17).

A rough criterion of the accuracy of a theory may be the ratio of the hyperfine coupling constants for positions 3 and 5 in the case of the benzyl radical, and for positions 1 and 3 in the case of the pentadienyl one. From Table 4 we see that the H-MO basis predicts in all cases a wrong order of these constants while for the SCH MO basis and formula (17) or (20) the agreement with experiment is almost quantitative.

We also note that it was sufficient to use a single value of Q for all the atoms and radicals, instead of the varying set as suggested by Zhidomirov and Schastnev [11].

In Tables 5 and 6 we compare the present results with those obtained by McLachlan and by other authors with more sophisticated methods. We see that the results of none of all the other methods are competitive with those obtained with the self consistent Hückel method and Eq. (17). It is particularly illuminating when comparing the hyperfine coupling constants for positions 3 and 5 in benzyl and for positions 1 and 3 in pentadienyl radicals (Table 6), or the relative error or maximum deviation in Table 5. We note that Adam and Laidlaw's SCF work [35], the best of all the other treatments, gives a relative error twice as large. The SCF CI method of Hinchliffe [37] yields a maximum deviation even 6 times larger.

Thus we conclude what follows:

1. In the case of benzyl, allyl, pentadienyl and perinaphthenyl neutral radicals formula (17) is much preferable; it is better founded than McLachlan's formula and gives a better agreement with experiment.

2. A proper consideration of the subtle differences in geometrical parameters is of a high importance and it happens that the selfconsistent Hückel method takes a much better account of these effects than the standard Hückel and all the advanced treatments applied hitherto to this problem.

3. It would be highly important to test these conclusions for a larger statistical material.

Finally we note that this discussion was concerned with neutral hydrocarbon radicals and that conclusions for charged radicals may happen to be different. We are in the course of an analysis of this problem.

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