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Spin Density Calculations in Semiempirical Restricted and Unrestricted SCF MO Methods

I. Spin Densities and Interaction Parameters in Various Quantum Chemical Methods

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In the present paper spin densities are calculated by ten methods on chosen radical systems. $\sigma - \pi$ interaction parameters for the individual methods are determined by McConnel's relation $a_i = Q\varrho_i$ and by that of Colpa-Bolton $a_i = (Q' + K\varepsilon_i)\,\varrho_i$ and the correlation between the results of the individual methods is studied.

In der vorliegenden Arbeit werden Spindichten anhand von zehn Methoden an ausgewählten Radikalsystemen ermittelt. Die $\sigma - \pi$-Kopplungsparameter für die einzelnen Methoden werden nach den McConnell $a_i = Q\varrho_i$- und Colpa-Bolton $a_i = (Q' + K\varepsilon_i)\,\varrho_i$-Beziehungen bestimmt. Die zwischen den Ergebnissen der einzelnen Methoden bestehende Korrelation wird untersucht.

Dans ce travail les densitées de spin sont calculées par dix méthodes sur un système des radicaux choisis. On détermine des parametres $\sigma - \pi$ d'interaction pour les méthodes individuelles dans la relation de McConnell $a_i = Q\varrho_i$ et celle de Colpa-Bolton $a_i = (Q' + K\varepsilon_i)\,\varrho_i$ et étudie la correlation entre les résultats des méthodes individuelles.

The interpretation of electron spin resonance spectra depends on the knowledge of spin densities, the relation of which to the hyperfine splitting constants is [1]

$$a_i = Q\varrho_{ii} \tag{1}$$

or for ion radicals [2]

$$a_i = (Q' + K\varepsilon_i)\,\varrho_{ii} \tag{2}$$

where ε_i are charge densities.

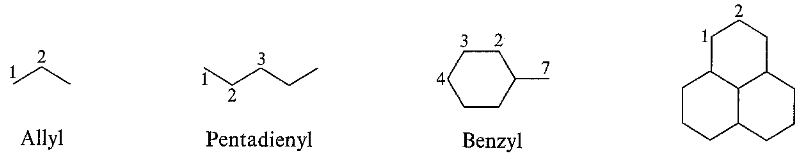
The $\sigma - \pi$ interaction parameters Q, Q' and K are taken as empirical parameters, ϱ_{ii} being the diagonal elements of the atomic spin density matrix [1].

To calculate the experimental values of splitting constants from the spin densities it is necessary to make a proper choice of interaction parameters; their uncritical application may result in false conclusions both on the method used and on the electron structure of the radical.

In the present paper spin densities for selected systems of radicals I, II and III respectively are calculated by various quantum-chemical methods. Appropriate $\sigma - \pi$ interaction parameters and their dependence on calculational methods of the spin densities are determined and the results of the individual methods are compared:

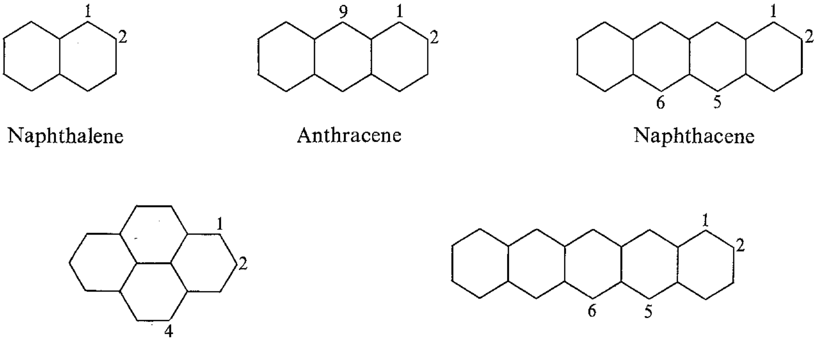
— HMO method,

— Method of Longuet-Higgins-Pople [3] with configuration interaction according to Lefebvre (LHP CI) [4].



Allyl Pentadienyl Benzyl Perinaphthenyl

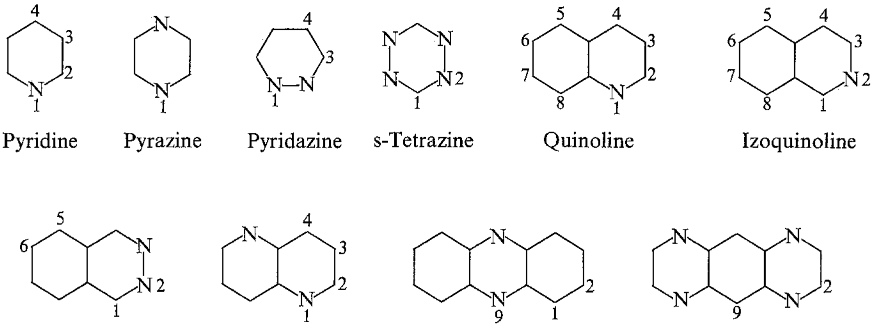
I



Naphthalene Anthracene Naphthacene

Pyrene Pentacene

II



Pyridine Pyrazine Pyridazine s-Tetrazine Quinoline Izoquinoline

Phthalazine 1,5-Diazanaphthalene Phenazine 1,4,5,8-Tetraazaanthracene

III

The ground configuration

$$^2\Psi_0 = |1\bar{1} \dots i\bar{i} \dots m\bar{m}n| \tag{3}$$

can interact with singly excited states of the form

$$^2\Psi_{i\to k} = \frac{1}{\sqrt{6}}\,[2|ik\bar{n}| - |i\bar{k}n| - |\bar{i}kn|] \tag{4}$$

where i, m, n and k are molecular orbitals with occupation numbers 2, 2, 1 and 0 respectively. When confining to the configuration interaction of monoexcited states one obtains a function which may be expressed by

$$\Psi = \Psi_0 + \sum_{ik} \lambda(i,k)\, \Psi_{i\to k} \tag{5}$$

and consequently [5]

$$\varrho_r = c_{nr}^2 + \frac{4}{\sqrt{6}} \sum_{ik} \lambda(i,k)\, c_{ir} c_{ik} - \frac{1}{6} \sum_{ik} \lambda^2(i,k)\, [4c_{ir}^2 + 4c_{kr}^2 - 2c_{nr}^2] \tag{6}$$

— HMO CI method.

Configuration interaction as in LPH CI method with HMO molecular orbitals only.

— Roothaan method [6] with configuration interaction as in LHP CI method (RTH CI).

— McLachlan method [7] with the parameter $\lambda = 1.2$ (McL).

— The Unrestricted Hartree-Fock [8] method (UHF-SD)[1].

— The UHF method arranged by Giacometti-Orlandi [11] (UHF GO).

The spin density on the r^{th} atom is

$$\varrho_r = c_{nr}^2 + \sum_{i=1}^{m} \left[\frac{1}{3} (c_{nr}^2 - c_{ir}'^2) - \frac{2}{3} c_{nr} c_{ir}' S_{ni'} \right] \tag{7}$$

where n denotes the MO occupied with the non-paired electron, c_{ir} and c_{ir}' are coefficients of the r^{th} AO in the i^{th} MO for electrons with α- or β-spin and $S_{ni'}$ is the overlap integral between the singly occupied MO and ψ_i'.

— The UHF method after complete projection according to Marschall [12] (UHF MSL).

Spin densities are calculated from the first two terms of formula (7) using the corresponding orbitals [13][2].

— The UHF method with complete projection of UHF wave function according to Harris [17].

Spin densities are calculated from the corresponding orbitals according to the formula

$$\varrho_r = \frac{1}{3 \sum_k \binom{n_\alpha}{k}^{-1} \Delta_k} \sum_j^{n_\alpha} \sum_k^{n_\beta} \binom{n_\alpha}{k}^{-1} \Delta_k^j \left[\frac{n_\alpha + k + 2}{n_\alpha - k} c_{jr}^2 - c_{jr}'^2 - 2 \frac{k+1}{n_\alpha - k} d_j c_{jr} c_{jr}' \right] \tag{8}$$

where $d_j = \langle x_j | x_j' \rangle$, n_α and n_β is the amount of electrons with α- and β-spin, resp.

From the auxiliary function

$$\Theta_p = \sum_{i=1}^{n_\beta} d_i^{2p}$$

we may, using the recurrent formula,

$$\Delta_k = \frac{1}{k} \sum_{p=1}^{k} (-1)^{p+1} \Delta_{k-p} \Theta_p$$

calculate Δ_k with the initial value $\Delta_0 = 1$.

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[1] This method was developped independently by Berthier [8] and Pople and Nesbet [9]. Application of this method to the hyperfine structure of ESR spectra was suggested by McConnell [10].

[2] The equations used represent a special case of the universal equation $a_r = \left(Q c_{0r}^2 + k \sum_i \varrho_i\right)$ including the contribution of the inner-shell π-spin densities to ESR proton splittings in planar π-radicals [14–16].

Δ_k^j may then be determined from the recurrent formula

$$\Delta_k^j = \Delta_k - d_j^2\, \Delta_{k-1}^j$$

with the initial value $\Delta_0^j = 1$.

Following the projection of the wave function the charge density is calculated from the relation

$$q_r = \frac{1}{\sum\limits_k \binom{n_\alpha}{k}^{-1} \Delta_k} \sum_j^{n_\alpha} \sum_k^{n_\beta} \binom{n_\alpha}{k}^{-1} \Delta_k^j \left[c_{jr}^2 + c_{jr}'^2 + 2 d_j c_{jr} c_{jr}'\right]. \tag{9}$$

— The UHF method with partial projection of the wave function according to Amos and Snyder [13] (UHF AS).

Spin densities within the group II and III were determined according to the approximative formula

$$\varrho_r = P_{ii} - Q_{ii} - 2/x\,(\boldsymbol{PQP} - \boldsymbol{QPQ})_{ii}$$

where $\boldsymbol{P}$ and $\boldsymbol{Q}$ are the bond order matrices for electrons with α and β spin and

$$x = (s'+1)(s'+2) - \tfrac{1}{4}(n_\alpha - n_\beta)^2 - \tfrac{1}{2}(n_\alpha + n_\beta) + \mathrm{Tr}\,\boldsymbol{PQ}$$

and

$$s' = \tfrac{1}{2}(n_\alpha - n_\beta).$$

Results and Discussion

The spin densities calculated by the individual methods, as well as the experimental values of the splitting constants, are shown in Table 1. In the calculations the following parameters were used: γ integrals were determined according to Pariser-Parr [18] with $\gamma_{ii}^{\mathrm{C}} = 11.13$ eV and $\gamma_{ii}^{\mathrm{N}} = 12.34$ eV [19, 20]. For adjacent positions $\beta_{ij}^{\mathrm{C-C}} = -2.39$ eV, $\beta_{ij}^{\mathrm{C-N}} = -2.74$ eV, $\beta_{ij}^{\mathrm{N-N}} = -2.35$ eV [19]; for the non-adjacent ones-zero. Atomic valence state ionization potentials W_i were put equal to zero and for nitrogen heterocompounds $\delta W_{\mathrm{N}} = (W_{\mathrm{N}} - W_{\mathrm{C}}) = -1.68$ eV.

Considering that in the radicals of alternating hydrocarbons $\varepsilon_i^+ = -\varepsilon_i^-$, we obtain from the formula (2)

$$a_i^{1/2} = \frac{a_i^+ + a_i^-}{2} = Q'\varrho_i$$

and

$$\frac{a_i^+ - a_i^-}{2} = K\varepsilon_i^+ \varrho_i = a_i^{1/2} - a_i^- = \Delta a_i^{1/2} \tag{10}$$

from which when using different ion radicals, we may determine Q' and K, or the Q'/K ratio

$$Q' = \frac{\sum\limits_i (a_i^+ + a_i^-)}{2\sum\limits_i \varrho_i}, \quad K = \frac{\sum\limits_i (a_i^+ - a_i^-)}{\sum\limits_i 2\varepsilon_i^+ \varrho_i}$$

Table 1. *Spin densities and experimental values of hyperfine splitting constants*

Radical	Position	HMO	LHP CI	HMO CI	RTH CI	MCL	UHF SD	UHF GO	UHF MSL	UHF UP	UHF AS	$a_E\,[G]^a$
Allyl	1	0.5000	0.5225	0.5275	0.6079	0.6061	0.6449	0.5483	0.5483	0.5449	0.5449	−14.38
	2	0.0000	−0.0449	−0.0550	−0.2158	−0.2121	−0.2898	−0.0966	−0.0966	−0.0898	−0.0898	4.06
Pentadienyl	1	0.3333	0.3332	0.3744	0.3727	0.4526	0.5288	0.3806	0.3767	0.3765	0.3762	− 8.99
	2	0.0000	−0.0383	−0.0502	−0.1523	−0.1567	−0.2890	−0.0964	−0.0963	−0.0894	−0.0889	2.65
	3	0.3333	0.4104	0.3516	0.5594	0.4103	0.5205	0.4317	0.4393	0.4260	0.4256	−13.40
Benzyl	2	0.1429	0.1693	0.1624	0.1072	0.1642	0.2464	0.1850	0.1532	0.1544	0.1543	− 5.10
	3	0.0000	−0.0186	−0.0226	−0.0535	−0.0752	−0.1489	−0.0555	−0.0497	−0.0474	−0.0473	1.60
	4	0.1429	0.1776	0.1734	0.1092	0.1352	0.2187	0.1777	0.1249	0.1268	0.1266	− 6.30
	7	0.5714	0.5570	0.5905	0.8604	0.8092	0.7666	0.6679	0.7280	0.7162	0.7162	−16.40
Perinaphthenyl	1	0.1667	0.1863	0.1917	—	0.2290	0.3268	0.2200	0.2200	0.2128	0.2164	− 7.30
	2	0.0000	−0.0208	−0.0268	—	−0.0725	−0.1943	−0.0648	−0.0648	−0.0578	−0.0614	2.20
Naphthalene±	1	0.1809	0.1972	0.1963	0.2235	0.2291	0.2578	0.2129	0.2129	0.2123	0.2130	− 5.54 − 4.90
	2	0.0691	0.0618	0.0633	0.0346	0.0428	0.0285	0.0492	0.0492	0.0494	0.0492	− 2.06 − 1.83
Anthracene±	1	0.0967	0.1096	0.1057	0.1092	0.1190	0.1369	0.1054	0.1057	0.1054	0.1055	− 3.12 − 2.76
	2	0.0483	0.0441	0.0454	0.0161	0.0310	0.0166	0.0344	0.0301	0.0303	0.0302	− 1.40 − 1.53
	9	0.1933	0.2060	0.2141	0.2649	0.2584	0.3111	0.2473	0.2563	0.2547	0.2561	− 6.65 − 5.41
Naphthacene±	1	0.0563	0.0647	0.0615	0.0433	0.0670	0.0767	0.0560	0.0555	0.0554	0.0552	− 1.72 − 1.55
	2	0.0336	0.0306	0.0333	0.0353	0.0213	0.0082	0.0207	0.0174	0.0176	0.0175	− 1.06 − 1.15
	5	0.1473	0.1617	0.1647	0.1784	0.1969	0.2469	0.1904	0.1953	0.1942	0.1952	− 5.17 − 4.25

Table 1 (continued)

Radical	Position	HMO	LHP CI	HMO CI	RTH CI	MCL	UHF SD	UHF GO	UHF MSL	UHF UP	UHF AS	a_E [G][a]
Pyrene$^-$	1	0.1358	0.1438	0.1583	0.1619	0.1892	0.2432	0.1661	0.1699	0.1693	0.1697	−4.75
	2	0.0000	−0.0158	−0.0216	−0.0163	−0.0541	−0.1231	−0.0411	−0.0410	−0.0395	−0.0399	1.09
	4	0.0873	0.0917	0.0899	0.0758	0.0926	0.0924	0.0886	0.0866	0.0856	0.0862	−2.08
Pentacene$^-$	1	0.0353	0.0404	0.0384	0.0271	0.0408	0.0453	0.0315	0.0308	0.0308	0.0305	−0.89
	2	0.0237	0.0214	0.0206	0.0184	0.0148	0.0033	0.0123	0.0101	0.0101	0.0101	−0.89
	5	0.1059	0.1193	0.1194	0.1112	0.1059	0.1749	0.1296	0.1309	0.1302	0.1304	−3.08
	6	0.1412	0.1563	0.1592	0.1784	0.1412	0.2596	0.1998	0.2065	0.2045	0.2058	−4.35
Pyridine$^-$	1/N/	0.3183	0.2986	0.3292	—	0.3704	0.3613	0.3065	0.3128	0.3128	0.3134	6.28
	2	0.1694	0.0781	0.1740	—	0.1824	0.0494	0.0730	0.0669	0.0670	0.0666	−3.14
	3	0.0312	0.0764	0.0078	—	0.0543	0.0347	0.0699	0.0625	0.0625	0.0621	−0.88
	4	0.2804	0.3925	0.3058	—	0.3621	0.4706	0.4102	0.4286	0.4279	0.4292	−9.10
Pyrazine$^-$	1/N/	0.3039	0.3288	0.3235	0.3504	0.3726	0.3989	0.3411	0.3545	0.3543	0.3551	7.21
	2	0.0980	0.0856	0.0883	0.0748	0.0568	0.0506	0.0802	0.0727	0.0729	0.0724	−2.64
Pyridazine$^-$	1/N/	0.3388	0.2450	0.3499	0.3008	0.4048	0.3170	0.2623	0.2681	0.2675	0.2685	5.90
	3	0.0157	−0.0205	−0.0069	−0.0944	−0.0703	−0.1201	−0.0380	−0.0382	−0.0385	−0.0392	0.16
	4	0.1457	0.2755	0.1570	0.2936	0.1522	0.3031	0.2760	0.2704	0.2693	0.2708	−6.47
S-tetrazine$^-$	1	0.0000	−0.0257	−0.0330	−0.1005	−0.1001	−0.1295	−0.0432	−0.0431	−0.0413	−0.0440	0.21
	2/N/	0.2500	0.2628	0.2665	0.3002	0.2917	0.3148	0.2716	0.2716	0.2707	0.2720	5.28
Quinoline$^-$	1/N/	0.2205	0.1603	0.2352	—	0.2467	0.2101	0.1711	0.1718	0.1713	0.1717	3.95
	2	0.1681	0.0709	0.1736	—	0.1913	0.0582	0.0706	0.0665	0.0666	0.0665	−3.29
	3	0.0383	0.0643	0.0136	—	−0.0305	0.0227	0.0555	0.0501	0.0503	0.0502	−1.26
	4	0.2459	0.2189	0.2669	—	0.3301	0.3001	0.2409	0.2512	0.2502	0.2514	−7.80
	5	0.1192	0.1992	0.1339	—	0.1623	0.2580	0.2070	0.2132	0.2124	0.2132	−3.90
	6	0.0301	0.0587	0.0223	—	−0.0073	0.0216	0.0508	0.0454	0.0456	0.0454	−1.14
	7	0.0724	0.0654	0.0793	—	0.0746	0.0359	0.0567	0.0521	0.0524	0.0522	−2.02
	8	0.0851	0.1939	0.0877	—	0.0869	0.2438	0.1991	0.1995	0.1989	0.1996	−3.46

Table 1 (continued)

Radical	Position	HMO	LHP CI	HMO CI	RTH CI	MCL	UHF SD	UHF GO	UHF MSL	UHF UP	UHF AS	a_E [G][a]
Phthalazine$^-$	1	0.2430	0.1963	0.2676	0.1740	0.3306	0.2221	0.1771	0.1788	0.1784	0.1788	– 5.91
	2/N/	0.0398	0.0457	0.0255	0.0465	0.0047	0.0134	0.0465	0.0381	0.0384	0.0381	0.88
	5	0.1450	0.2098	0.1566	0.2492	0.1822	0.2961	0.2430	0.2491	0.2482	0.2492	– 4.64
	6	0.0664	0.0634	0.0635	0.0499	0.0437	0.0353	0.0595	0.0553	0.0553	0.0553	– 2.14
Izoquinoline$^-$	1	0.2893	0.2091	0.3002	—	0.3918	0.2686	0.2204	0.2251	0.2243	0.2252	– 5.38
	2/N/	0.1758	0.0543	0.1896	—	0.1770	0.0399	0.0560	0.0516	0.0518	0.0516	1.92
	3	0.0001	0.0488	0.0024	—	–0.0603	–0.0021	0.0322	0.0294	0.0297	0.0294	– 0.37
	4	0.1151	0.1873	0.1309	—	0.1274	0.2444	0.1950	0.1967	0.1962	0.1967	– 4.01
	5	0.0985	0.1969	0.1002	—	0.0924	0.2425	0.2044	0.2050	0.2042	0.2050	– 3.95
	6	0.1071	0.0739	0.1181	—	0.1245	0.0659	0.0764	0.0718	0.0719	0.0718	– 3.26
	7	0.0213	0.0512	0.0069	—	–0.0334	–0.0049	0.0359	0.0314	0.0318	0.0314	– 0.04
	8	0.1616	0.2084	0.1794	—	0.2274	0.2860	0.2266	0.2345	0.2337	0.2346	– 6.26
1,5-Diazanaphthalene$^-$	1/N/	0.1723	0.1618	0.1885	0.1877	0.2129	0.2116	0.1701	0.1730	0.1725	0.1729	3.37
	2	0.1066	0.0712	0.1090	0.0481	0.1021	0.0485	0.0662	0.0613	0.0614	0.0614	– 2.95
	3	0.0517	0.0669	0.0408	0.0540	0.0175	0.0330	0.0601	0.0548	0.0550	0.0550	– 1.69
	4	0.1596	0.2163	0.1711	0.2238	0.1990	0.2846	0.2302	0.2365	0.2360	0.2367	– 5.77
Phenazine$^-$	1	0.0455	0.1118	0.0468	0.1116	0.0489	0.1213	0.0958	0.0965	0.0956	0.0965	– 1.80
	2	0.0396	0.0399	0.0407	0.0222	0.0248	0.0277	0.0414	0.0376	0.0377	0.0377	– 1.54
	9/N/	0.2627	0.1834	0.2847	0.2241	0.3415	0.2651	0.2151	0.2231	0.2220	0.2229	5.15
1,4,5,8-Tetraazaanthracene$^-$	1/N/	0.1314	0.1003	0.1451	0.0842	0.1583	0.1299	0.0995	0.1002	0.0999	0.1000	2.41
	2	0.0730	0.0573	0.0720	0.0333	0.0600	0.0398	0.0507	0.0458	0.0459	0.0460	– 2.73
	9	0.0910	0.2063	0.1026	0.2736	0.1192	0.3049	0.2404	0.2491	0.2474	0.2488	– 3.96

[a] From [23, 24, 26].

Table 2. *Interaction parameters Q', K and their relation for individual methods*

Method	Q'	K	Q'/K
HMO	35.62	16.78	2.122
HMO CI	31.50	16.86	1.868
McL	25.05	18.37	1.364
RTH CI	24.87	14.55	1.709
LHP CI	32.03	17.58	1.822
UHF SD	20.43	10.60	1.927
UHF UP	28.55	12.69	2.249
UHF GO	28.03	12.85	2.181
UHF MSL	27.95	12.66	2.208
UHF AS	28.50	12.66	2.251

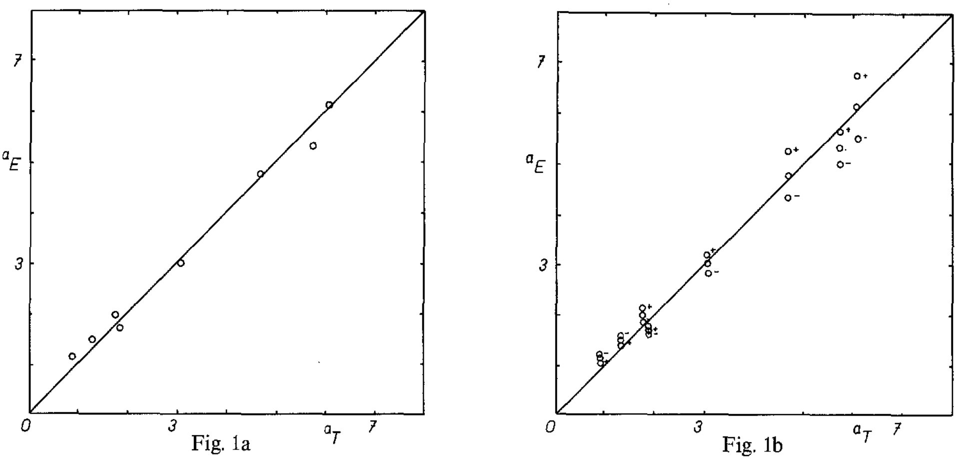

Fig. 1a

Fig. 1b

Fig. 1. a) Dependence of experimental values of splitting constants $a_E^{1/2} = (a^+ + a^-)/2$ on those calculated for naphtalene, anthracene and tetracene in the LHP CI method. b) Dependence of experimental values of splitting constants $(a^{1/2})$ on the calculated $(a_T 0)$. Maintaining the same a_T values, also the appropriate $a_E^+(0+)$ and $a_E^-(0-)$ values are plotted

and

$$\frac{Q'}{K} = \frac{\sum_i (a_i^+ + a_i^-)}{\sum_i (a_i^+ - a_i^-)} \cdot \frac{\sum_i \varepsilon_i^+ \varrho_i}{\sum_i \varrho_i}. \tag{11}$$

The values of these constants in the individual methods for the ion radicals of naphthalene, anthracene and tetracene, as well as the Q'/K ratio are shown in Table 2[3].

As may be seen in Table 2, the interaction parameters of the individual methods differ from each other, the Q'/K quotient being within the range of the 2.11 value known from the literature [22, 23].

For the $a^{1/2}$ value the McConnell's relation (1) proves to be well satisfied (Fig. 1a). The absolute value of the second term in (2), is equal for both the anion

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[3] For the splitting constants of group I radicals and the $a^{1/2}$ values of the three ion radicals of group II, the Q' values were determined by the method of least squares.

Table 3. *Theoretical and experimental $a^{1/2}$ values*

System	Atom	a_i^+	a_i^-	$a_i^{1/2}$	$\Delta a_i^{1/2}$	ε_i^+	ϱ_i	$K\varepsilon_i\varrho_i$
Naphthalene	1	5.54	4.90	5.220	0.320	0.192	0.197	0.596
	2	2.06	1.83	1.945	0.115	0.086	0.061	0.095
Anthracene	1	3.12	2.76	2.940	0.180	0.115	0.106	0.221
	2	1.40	1.53	1.456	−0.065	0.064	0.045	0.048
	9	6.65	5.41	6.030	0.620	0.214	0.209	0.774
Naphthacene	1	1.72	1.55	1.635	0.085	0.065	0.065	0.074
	2	1.06	1.15	1.105	−0.045	0.070	0.031	0.038
	5	5.17	4.25	4.710	0.460	0.164	0.162	0.466

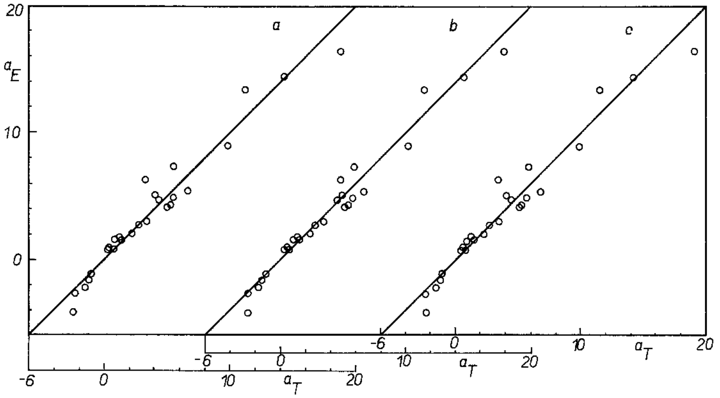

Fig. 2. Dependence of the experimental values of splitting constants in groups I and II of the radicals on those calculated in UHF UP, UHF GO and UHF MSL methods respectively

and cation radical; from both the Table 3 and Fig. 1b it is seen that the second term quite correctly demonstrates the deviations of $\Delta a_i^{1/2}$ from the $a_i^{1/2}$ [4] value.

Both constants Q' and K (Table 2), thus determined shall now be applied to all the groups. The statistical parameters, shown in Table 4, refer to the results obtained according to the individual methods. Apart from the current values, we use that of SE* characterizing the standard error with respect to the line passing through the origin.

This value, together with the abscissa on the perpendicular axis, tells us how the corresponding method satisfies McConnell's or Colpa-Bolton's relation. In Table 4 we separated the first two groups of radicals because of the facts derived from the results (Fig. 3). In the third group of radicals, we obtained a relatively poor correlation[5], which may not be considerably improved chosing other parameters in the calculation of spin densities; similar results were obtained also by Black and McDowell [24] within all of the three versions of parameters choice used[6]. Spin densities in nitrogen atoms we correlated with corresponding splitting constants according to McConnell's relation (1) and with the interaction para-

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[4] In two positions (anthracene-2 and tetracene-2), the experimental deviations have reverse signs with respect to the theoretical ones.

[5] Similar results may even then be obtained when the interaction parameters are determined by the method of least squares referring for the present group of radicals.

[6] In heterocompounds, as referred to by Melchior [25], the contribution of σ bonds, adjacent to C atom, may be a considerable one with which the discrepance obtained might well be cleared.

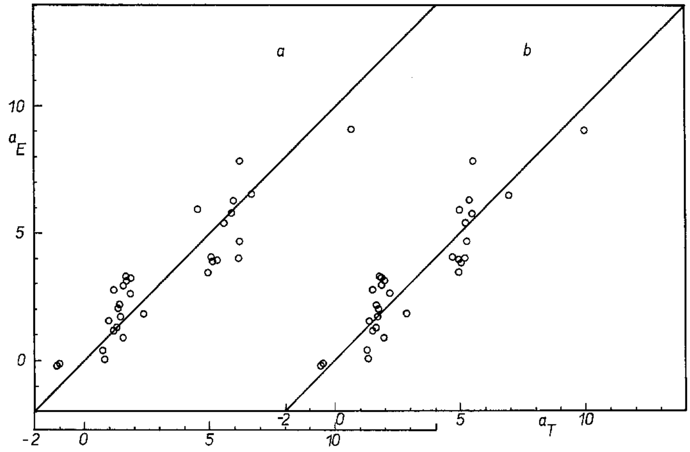

Fig. 3. Dependence of the experimental values of splitting constants in groups III of the radicals on those calculated in UHF UP and LHP methods respectively

meters shown in Table 4. This correlation, compared with the preceding one, proves to be a good one.

For each method we used the Q' and K constants individually. The individual methods show different distributions of spin densities bringing about different interaction parameters as well. The most remarquable difference is between the parameters of the group I radicals in the UHF SD ($Q = -19.73$ G) and HMO ($Q = -37.61$ G) methods respectively; therefore the parameters should carefully be chosen with respect to the spin density calculations. In the UHF method with the projection of the UHF wave function, the spin densities (Table 1) and, consequently, the interaction parameters (Table 2) as well, are very close to each other and therefore, the conclusion may be drawn, that the simple UHF GO and UHF MSL methods give results comparable with those of the UHF UP (Fig. 2) method. The results obtained by the UHF AS method (though for radicals with a greater number of atoms a simplified formula was used) differ unconsiderably from those obtained by the UHF UP (Table 1)[7] method.

Although the interaction parameters are commonly thought to be appliable on any radicals and positions whatever, their choice does not appear to be a unambiguous one because of the fact that their values depend on the spin density calculation methods. As may be seen in Table 4, the application of individual constants for individual methods does not bring about any considerable differences in the results of the individual methods. The methods showing a poorer electronic correlation are referred to by the abscissa and the SE* respectively.

Snyder and Amos [23] suggest that the Q' value depends on the number of carbon atoms the central atom is bound to. From the Table 1, a further fact may be deduced which is the result of the unsufficient inclusion of the electronic correlation in some methods. Within these methods, the negative spin densities are very low and there have special values of interaction parameter Q' to be used for

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[7] Bloor *et al.* [22] used the restricted Hartree-Fock method for calculation of spin densities. Both the correlation coefficients and the interaction parametres of his method and of the UHF AS method are very close to each other [22a].

Table 4. *Parameters of the statistical analysis of the relation between the experimental values of splitting constants and spin densities*

Method	Radicals	Atom	c[a]	Standard error	Standard error*	Correlation coefficient
HMO	I + II	C	−0.543	0.411	1.729	0.959
	III	C	0.240	0.964	1.064	0.907
		N	−0.426	0.708	0.729	0.938
	I + II + III	C	−0.141	1.224	1.402	0.946
HMO CI	I + II	C	−0.309	1.071	1.194	0.977
	III	C	0.551	0.871	0.939	0.925
		N	−0.305	0.729	0.740	0.934
	I + II + III	C	0.116	1.016	1.064	0.963
McL	I + II	C	0.727	1.174	1.389	0.972
	III	C	1.489	0.934	1.549	0.914
		N	0.181	0.654	0.659	0.948
	I + II + III	C	0.989	1.150	1.482	0.953
RTH CI	I + II	C	0.895	1.091	1.499	0.976
	III	C	1.479	0.876	0.964	0.903
		N	0.206	0.414	0.428	0.983
	I + II + III	C	1.044	1.051	1.484	0.968
LHP CI	I + II	C	−0.433	0.882	1.042	0.984
	III	C	1.539	0.916	1.095	0.917
		N	0.556	0.456	0.542	0.975
	I + II + III	C	−0.267	0.929	1.071	0.969
UHF GO	I + II	C	−0.87	0.799	0.870	0.987
	III	C	0.554	0.916	1.030	0.917
		N	0.450	0.333	0.417	0.987
	I + II + III	C	0.224	0.886	0.954	0.972
UHF MSL	I + II	C	0.260	1.192	1.192	0.977
	III	C	0.679	0.915	1.074	0.917
		N	0.613	0.291	0.441	0.990
	I + II + III	C	0.379	0.999	1.129	0.964
UHF UP	I + II	C	0.209	1.083	1.235	0.976
	III	C	0.671	0.914	1.104	0.917
		N	0.613	0.291	0.443	0.990
	I + II + III	C	0.341	1.018	1.166	0.963
UHF AS	I + II	C	0.209	1.079	1.229	0.976
	III	C	0.685	0.914	1.112	0.917
		N	0.618	0.290	0.445	0.990
	I + II + III	C	0.345	1.018	1.167	0.963
UHF SD	I + II	C	0.963	0.989	1.292	0.980
	III	C	1.333	0.967	1.381	0.907
		N	0.820	0.294	0.556	0.990
	I + II + III	C	1.070	1.001	1.343	0.964

[a] From the relation $y = kx + c$.

Table 5. *Values of interaction parameters differentiated for various positions in the group I of radicals*

Method	Position[a]	Q
HMO	a	—
	b	28.31
	c	40.85
LHP CI	a	85.72
	b	28.15
	c	34.02
HMO CI	a	67.98
	b	26.65
	c	36.51
RTH CI	a	19.71
	b	21.60
	c	31.97
McL	a	20.35
	b	21.29
	c	34.20
UHF SD	a	11.40
	b	20.50
	c	24.46
UHF GO	a	33.55
	b	24.91
	c	31.64
UHF MSL	a	34.19
	b	24.06
	c	34.24
UHF UP	a	36.95
	b	24.29
	c	34.89
UHF AS	a	36.57
	b	24.29
	c	34.78

[a] a: Positions with negative spin densities; b: Positions having two carbons bonded to the central sp^2 carbon; c: Positions having only one carbon bonded to the central sp^2 carbon.

them. When calculating the splitting constants for the first group of radicals, in classifying the positions into those groups, we obtain quite an excellent accordance with the experiment for all the methods used (Table 5, Fig. 4). The differences of the Q' values prove to be particularly great in the HMO and LHP CI methods; they do decrease, however, in passing over to more exact ones.

In the group of the restricted Hartree-Fock methods, the LHP CI method proves to be quite a good one. Using it, it should, however, be considered, that small negative spin densities are obtained (Table 5). Within the statistical evaluation, the RTH CI method gives somewhat poorer results; it shows, however, better the positions with negative spin densities. In these methods the ratio of spin densities at para and ortho positions of benzyl radical is higher than 1 in

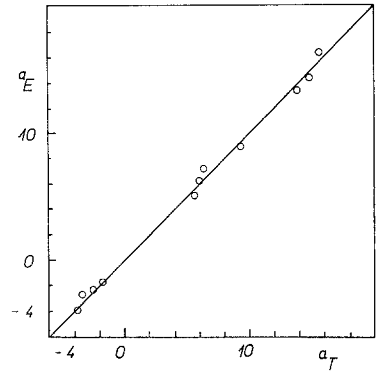

Fig. 4. Dependence of the experimental values of splitting constants in groups III of the radicals on those calculated in the UHF UP and LHP CI methods respectively

Table 6. *Charge densities in* UHF SD *and* UHF UP *methods*

Radical	Position	UHF SD	UHF UP
Naphthalene$^-$	1	1.1882	1.1883
	2	1.0935	1.0927
Anthracene$^-$	1	1.0965	1.0961
	2	1.0851	1.0847
	9	1.2140	1.2148
Pyrene$^-$	1	1.1582	1.1593
	2	1.0052	1.0055
	4	1.0983	1.0978
Naphthacene$^-$	1	1.0509	1.0503
	2	1.0746	1.0740
	5	1.1676	1.1682
Pentacene$^-$	1	1.0278	1.0274
	2	1.0648	1.0643
	13	1.1747	1.1758
	14	1.1177	1.1174
Pyridine$^-$	2	1.0875	1.0859
	3	1.1240	1.1229
	4	1.2808	1.2840

agreement with the experiment, while in UHF methods this ratio is lower than 1. By symmetrization of the wave function within the group of unrestricted Hartree-Fock methods the spin densities change considerably, whereas in the charge densities the changes are small (Table 6). We obtained good results in the simple UHF GO method, though the differences of spin densities (particularly among the further three methods) are very small irrespective of which one is used.

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