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Relationes

A Modification of McLachlan Method for Spin Density Calculations

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A modification of McLachlan theoretical method for spin density calculations, which uses radical polarisabilities instead of cation ones, improves significantly its agreement with experiment.

Key words: Spin density distribution, McLachlan modified method for calculating ~

The method of McLachlan [1] (*ML*) is a perturbation treatment of UHF hamiltonian in the formalism of Brickstock and Pople [2]. Owing to its simplicity and flexibility, it is still used by chemists, mainly for large radicals. Moreover, it surprisingly often gives more valuable results than rigorous methods, for example for benzyl radical (reviews: [3, 4]; see also Ref. [5]). The basic formula of ML method for the spin density ϱ_μ on atom μ is:

$$\varrho_\mu = C_{n\mu}^2 + \sum_{r=1}^{n-1} C_{r\mu}'^2 - C_{r\mu}^2 \tag{1}$$

in which the $C'_{r\mu}$ are solutions of the modified Hückel determinant:

$$\Delta H_{\mu\nu} = F_{\mu\nu}^{\alpha} - F_{\mu\nu}^{\beta} . \tag{2}$$

Relation 1 is also the charge variation on atom μ for the cation of the radical considered, so ML gives another formula including the polarisabilities of Coulson and Longuet-Higgins [6]

$$\varrho_\mu = C_{n\mu}^2 + \sum_\nu \pi_{\mu\nu} \Delta H_{\nu\nu} + \sum_{\nu,\sigma} \pi_{\mu,\nu\sigma} \Delta H_{\nu\sigma} \tag{3}$$

the two formulations of ML method are

$$\begin{array}{l} \text{method } \Delta\alpha \quad : \text{Eq. (1)} \\ \text{method POL 1: Eq. (3)} \end{array} \quad \text{with} \quad \begin{cases} \Delta H_{\nu\nu} = 2\lambda\beta C_{n\nu}^2 \\ \Delta H_{\mu\nu} = 0 . \end{cases}$$

In POL 1 method, atom-atom polarizabilities $\pi_{\mu\nu}^1$ are those of the corresponding cation of the radical studied

$$\pi_{\mu\nu}^1 = 4 \sum_{r=1}^{n-1} \sum_{s=n}^{2n-1} \frac{C_{r\mu} C_{r\nu} C_{s\mu} C_{s\nu}}{E_r - E_s} .$$

Table 1. Comparison of the two methods of ML

Allyl radical p_1			Naphtalene anion		
λ	$\Delta\alpha$	POL 1	$\lambda=1.2$	$\Delta\alpha$	POL 1
0.1	0.50883	0.50884	ϱ_1	0.22912	0.22915
0.6	0.55188	0.55303	ϱ_2	0.04290	0.04280
1.2	0.59764	0.60607	ϱ_g	−0.04405	−0.04395

In his original paper, ML only used POL 1. The two formulations of ML are often believed as "entirely equivalent" [7, 8]. However, Nowakowski [4] noted that they give very different results for neutral radicals. This is not unexpected since POL 1 is a first order approximation of $\Delta\alpha$: the two methods are equivalent as far as the perturbing terms $2\lambda C_{n\mu}^2$ are small. Table 1 clearly illustrates this situation by variation of λ.

Starting from Hückel orbitals as zero order approximation, we apply Brickstock and Pople equations to a neutral alternant radical: after the first iteration, the spin density variation on atom μ is equal to the charge variation in the radical itself (instead of the cation for ML):

$$\text{POL 2: } \varrho_\mu = C_{n\mu}^2 + \textstyle\sum_\nu \pi_{\mu\nu}^2 C_{n\nu}^2 \,. \tag{4}$$

Table 2. Spin densities and hyperfine splitting of some neutral

			λ	POL 1			POL 2		
	Ref.	a_μ^{exp}		ϱ_μ	a_μ^{th}	Q σ	ϱ_μ	a_μ^{th}	Q σ
Benzyl	[3]	16.35	1	0.77	17.25		0.62	16.52	
		5.14		0.161	3.60	22.41	0.201	5.36	26.62
		1.75		−0.063	1.40		−0.063	1.67	
		6.14		0.137	3.06	1.79	0.205	5.45	0.374
Planar	[11]	12.7	1	0.534	13.02		0.449	12.57	
diphenylmethyl		3.41		0.129	3.13	24.37	0.139	3.90	28.00
(xanthyl)		0.94		−0.043	1.04		−0.043	1.19	
		4.06		0.119	2.8	0.623	0.140	3.91	0.294
Diphenylmethyl	[12]	14.7		0.726	15.13		0.50	14.62	
$\beta_{12}=0.92$		3.7	1.2	0.122	2.95	24.12	0.139	4.06	29.27
		1.35		−0.048	1.16		−0.048	1.41	
(23°)		4.2	23°	0.109	2.64	0.9	0.140	4.10	0.191
Triphenylmethyl	[13]	2.57	1.2	0.096	2.81		0.104	2.71	
$\beta_{12}=0.87$		1.13		−0.036	1.05	29.28	−0.036	0.94	26.14
(30°)		2.81	30°	0.088	2.59	0.193	0.104	2.73	0.146

$\pi^2_{\mu\nu}$ is the atom-atom polarizability of the radical and $\pi^2_{\mu,\nu\sigma} \equiv 0$ for a neutral alternant. It is easy to show that:

$$\pi^2_{\mu\nu} = 4\sum_{r=1}^{n-1}\sum_{s=n}^{2n-1} \frac{C_{r\mu}C_{r\nu}C_{s\mu}C_{s\nu}}{E_r-E_s} + 2\sum_{r\neq n}\frac{C_{n\mu}C_{n\nu}C_{r\mu}C_{r\nu}}{E_n-E_r}.$$

POL 2 has been applied to calculate spin densities ϱ_μ, hyperfine splitting constants $a^{\text{th}}_\mu = Q\varrho_\mu$ and compared to McLachlan POL 1 or $\Delta\alpha$. The McConnell constant Q is chosen to minimize the standard deviation σ of $(a^{\text{exp}}_\mu - Q\varrho_\mu)$ measured for non equivalent experimental splittings. Agreement with experiment, characterized by σ, is always better for POL 2 than for POL 1 or $\Delta\alpha$ ($\Delta\alpha$ results, worse than POL 1 ones, are not reported in Table 2). Moreover, POL 2 gives ϱ ortho $< \varrho$ para for arylmethyl type radicals and value of Q agree better with the "good" value for neutral radicals ($Q \sim 27$G[9]).

Formula 4 of POL 2, only strictly true for neutral alternant, remains valid for anions or non-alternant if, like ML, we neglect nondiagonal terms in formula 3. Table 2 shows that POL 2 also improves agreement with experiment.

Validity of ML method has been discussed among others, by ML himself and by A.T. Amos [10]. Several authors proposed to modify it when applied to neutral [4a] ionic alternant or not [8, 4b] radicals. Our POL 2 modification of ML method, while keeping it simple, improves its validity.

alternant (left) and neutral nonalternant or ionic (right) radicals

			λ	POL 1			POL 2		
	Ref.	a^{exp}_μ		ϱ^{th}_μ	a^{th}_μ	Q σ	ϱ^{th}_μ	a^{th}_μ	Q σ
fluorenyl	[14]	13.49	1.2	0.568	13.77		0.450	13.58	
$\beta_{12}=\beta_{28}$		0.8		−0.024	0.60	24.22	−0.019	0.57	30.19
$=0.95$		3.90		0.097	2.36		0.119	3.60	
		0.6		−0.016	0.38	0.80	−0.004	0.11	0.31
xanthyl	[11]	12.73	1	0.507	12.97		0.42	12.54	
$h_O=2$		3.425		0.138	3.52	25.59	0.143	4.22	29.61
$k_{CO}=0.8$		0.988		−0.037	0.96		−0.035	1.04	
[11]		4.047		0.114	2.92	0.533	0.130	3.84	0.409
		0.89		−0.023	0.59		0.018	0.54	
thioxanthyl	[15]	11.82	1	0.51	12.10		0.426	11.70	
$h_S=1.6$		3.20		0.136	3.22	23.72	0.141	3.87	27.44
$k_{SC}=0.65$		1.07		−0.039	0.92		−0.037	1.02	
[16]		1.07		−0.028	0.67	0.549	−0.024	0.67	0.372
naphtalene	[7]	4.90	1	0.221	5.06	22.87	0.216	5.05	23.35
anion		1.82		0.047	1.08	0.536	0.052	1.22	0.438
anthracene	[7]	2.74	1	0.115	2.57		0.119	2.81	
anion		1.51		0.034	0.76	22.30	0.039	0.92	23.55
		5.34		0.248	5.52	0.458	0.229	5.40	0.348

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