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An Omega Technique Study of Proton Hyperfine Coupling Constants

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An extension of the ω-technique to open shell molecules is made, using the UHF formulation. Sample calculations are reported for a range of organic σ and π radicals, ions and lowest triplet states. The agreement with experiment is as good as that given by semi-empirical methods. Annihilation of the next highest spin function is often sufficient to improve the wavefunction, although in some cases the value $\langle S^2 \rangle_{\text{ASA}}$ is still inacceptably large.

Im Rahmen der UHF-Theorie wird die ω-Technik auf Moleküle mit offenen Schalen ausgedehnt. Die Übereinstimmung der Rechnungen für einige σ- und π-Radikale, Ionen und Triplettzustände mit dem Experiment ist wie üblich bei semiempirischen Methoden. Abspaltung des nächsthöheren Spinanteils ist meistens ausreichend, obwohl in manchen Fällen der $\langle S^2 \rangle$-Wert dann immer noch beträchtlich groß ist.

Extension de la technique ω aux molécules à couches ouvertes dans le cadre de la méthode U.H.F. Des calculs iolustratifs sont données pour une série de radicaux π et σ, d'ions et d'états triplets les plus bas. L'accord avec l'expérience est aussi bon que celui donné par les méthodes semi-empiriques. L'annihilation de la fonction de spin immédiatement supérieure est souvent suffisante pour améliorer la fonction d'onde, quoique dans certains cas la valeur S^2 ASA soit toujours trop grande.

1. Introduction

In many instances, the Hückel Molecular Orbital (HMO) method is sufficient to give a fair understanding of the gross features of spin density distributions in large organic molecules; McLachlan's λ-method [1] is a simple improvement, allowing for correlation between electrons of different spins, in a semi-empirical way. In this publication, we report another *simple* method for calculating spin density distributions, based on the ω-technique [2], but using the Unrestricted Hartree Fock (UHF) method explicitly. The method enjoys all the advantages of the UHF method, but suffers from all its shortcomings [3].

2. Method

We assume that the π-molecular orbitals of an open shell conjugated molecule, with p α electrons and q β electrons ($p > q$) have LCAO expansions with basis χ, so that

$$\boldsymbol{\Phi}^{\alpha} = \chi \boldsymbol{T}^{\alpha} ; \qquad \boldsymbol{\Phi}^{\beta} = \chi \boldsymbol{T}^{\beta} \tag{1}$$

in the usual sense [4]. The space parts of the one electron density matrix have (matrix) representations $\boldsymbol{P}$ and $\boldsymbol{Q}$, where, for example:

$$\boldsymbol{P} = \boldsymbol{T}^{\alpha} (\boldsymbol{T}^{\alpha})^{\dagger} \tag{2}$$

and the spinless, one electron, total charge and spin density functions are given by

$$\begin{aligned} P_1(1;1') &= \sum_{r,s} \chi_r(1)\,(P+Q)_{rs}\,\chi_s^*(1') \\ Q_1(1;1') &= \sum_{r,s} \chi_r(1)\,(P-Q)_{rs}\chi_s^*(1') \end{aligned} \tag{3}$$

respectively. Then using the current Zero Differential Overlap (ZDO) approximation [5], we may write down the r^{th} diagonal element of the UHF Hamiltonian matrix for the α electrons (say)

$$h_{rr}^{\alpha} = \omega_r + \sum_{t \neq r} (P_{tt} + Q_{tt} - Z_t)\,\gamma_{rt} + Q_{rr}\,\gamma_{rr} \tag{4}$$

in the usual notation, with an analogous equation for the β electrons.

For a closed shell molecule, $\boldsymbol{P} = \boldsymbol{Q} = \boldsymbol{R}$, say, and (4) reduces to

$$h_{rr} = \omega_r + \sum_{t \neq r} (2R_{tt} - Z_t)\,\gamma_{rt} + R_{rr}\,\gamma_{rr}\,. \tag{5}$$

Assuming that the third term in (5) is much larger than the second (often a good approximation; for an even alternant closed shell molecule, the second term is zero) then we may write

$$h_{rr} \approx (\omega_r + \tfrac{1}{2}\gamma_{rr}) - (1 - 2R_{rr})\frac{\gamma_{rr}}{2} \tag{6}$$

which is just the r^{th} diagonal element of the 'ω technique' Hamiltonian matrix, $\boldsymbol{h}^{\omega}$ [2];

$$h_{rr}^{\omega} = \alpha_0 + \beta_0\omega(1 - 2R_{rr})\,. \tag{7}$$

Applying the above approximation to (4) gives

$$\begin{aligned} h_{rr}^{\omega\alpha} &= \alpha_0 + \omega\beta_0(1 - 2Q_{rr}) \\ h_{rr}^{\omega\beta} &= \alpha_0 + \omega\beta_0(1 - 2P_{rr}) \end{aligned} \tag{8}$$

and we assume that the off diagonal elements of these matrices are given by

$$h_{rs}^{\omega i} = \begin{cases} \beta_0 & \text{if } r \text{ is bonded to } s \\ & (i = \alpha, \beta\,) \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

Eq. (8) are the usual coupled equations for the iterative construction of the self consistent density matrices $\boldsymbol{P}$ and $\boldsymbol{Q}$, and may be solved by either repeated diagonalisations, or by a 'Steepest Descent' procedure [6].

So far, we have limited our discussion to π radicals: however, the ZDO approximations have been applied to σ systems [7], where Eq. (8) can also be applied: in fact, such calculations have recently been reported for closed shell molecules [20].

In either case, the resultant wavefunction is not necessarily an eigenfunction of S^2, although it is automatically an eigenfunction of S_z, with eigenvalue $\frac{1}{2}(p - q)$. The mean value of S^2, $\langle S^2 \rangle$, may be improved by annihilating the next highest spin multiplet, after the manner of AMOS and SNYDER [3].

In the next sections, we present illustrative results for a number of doublet and triplet ions and radicals, including some σ radicals.

All the calculations were performed on the ICT 'Atlas' computer at Chilton, Berkshire, using a Fortran IV program. Convergence was good in every case, using repeated diagonalisations of the Hamiltonian matrices. The largest change in $\boldsymbol{P}$ and $\boldsymbol{Q}$ was, an average, 0.00001 after 15 cycles.

3. Results

In Fig. 1, we show the molecules on which the calculations were performed, together with the numbering systems. For convenience, we discuss the results in three parts. Tab. 1 contains the values of the mean value of S^2 before and after annihilation of the next highest spin multiplet, denoted by $\langle S^2\rangle_{SD}$ and $\langle S^2\rangle_{ASA}$ respectively.

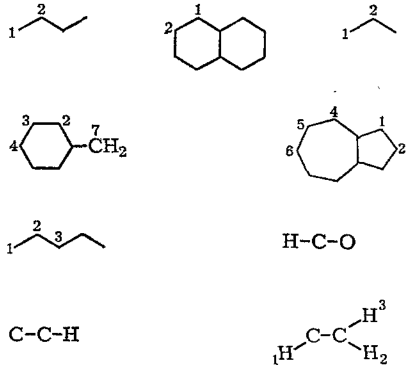

Fig. 1. Molecules studied

Table 1. *Mean Values of S^2 before and after annihilation*

Molecule	$\langle S^2\rangle_{SD}$	$\langle S^2\rangle_{ASA}$
butadiene$^-$	0.89129	0.75000
allyl	1.04943	0.75000
naphthalene$^-$	0.82481	0.75424
pentadienyl	1.40065	0.98890
azulene$^-$	1.34467	0.96585
benzyl	1.46293	1.20757
naphthalene*	2.12980	2.00652
butadiene*	2.00000	2.00000
formyl	0.75244	0.75000
ethynyl	0.75246	0.75000
vinyl	0.76357	0.75009

It is probable that the spin densities computed after single annihilation are more correct [8], and so we have adopted the course of presenting the charge densities, and the spin densities before and after single annihilation, but have only used the spin densities after annihilation to calculate observables.

Conjugated Radicals and Ions

The value $\omega = 1.4$ was used throughout this section. In Tab. 2, we present the results for allyl, pentadienyl, benzyl, butadiene anion and naphthalene anion. To compute coupling constants, we have used

(i) a simple MCCONNELL relationship [9]

$$a_i = -27\,\varrho_{ii}\ [\text{gauss}]$$

where $\varrho = \frac{1}{2M_s}(\boldsymbol{P} - \boldsymbol{Q})$ is the normalised spin density matrix, M_s being the spin quantum number

(ii) the expression

$$a_{ii} = -27\,\varrho_{ii} - 12.8\,\varepsilon_i\,\varrho_{ii}$$

due to COLPA and BOLTON [10], where ε_i is the usual 'excess charge'. These values also allow direct comparison with other calculations.

The calculated values for allyl are in excellent agreement with experiment [11], and also in good agreement with other SCF calculations (e.g. [3]). The values for naphthalene anion [12] are also in quite good agreement with experiment, but show the common failing of semi-empirical calculations, that the coupling constant for position 2 is too small. This probably means that a value different from -27

Table 2. *Doublets studied.* P_{ii}, $(\varrho_{ii})_{\mathrm{SD}}$, $(\varrho_{ii})_{\mathrm{ASA}}$ *are the* i^{th} *diagonal elements of the charge density and spin density matrices before and after annihilation*; a_i, a_{ii} *are the coupling constants calculated using relation (i), (ii),* a_{exp} *are the observed coupling constants (in* Gauss)

Molecule	atom	P_{ii}	$(\varrho_{ii})_{\mathrm{SD}}$	$(\varrho_{ii})_{\mathrm{ASA}}$	a_i	a_{ii}	a_{exp}
butadiene⁻	1	1.2517	+ .5996	+ .4810	−12.99	−11.44	− 7.62
	2	1.2484	− .0996	+ .0190	− 0.51	− 0.45	− 2.79
allyl	1	1.0	+ .7736	+ .5828	−15.39		−14.38
	2	1.0	− .5472	− .1657	+ 4.46		+ 4.06
naphthalene⁻	1	1.1372	+0.3084	+0.2349	− 6.34	− 5.93	− 4.90
	2	1.0964	− .0001	+ .0333	− 0.89	− 0.85	− 1.89
pentadienyl	1	1.0	+ .7535	+ .4734	−12.79		− 8.99
	2	1.0	− .5580	− .1598	+ 4.32		+ 2.65
	3	1.0	+ .6090	+ .3727	−10.06		−13.40
azulene⁻	1	1.1515	+0.1643	+0.0705	− 1.90	− 1.77	+ 0.27
	2	1.1719	−0.0082	+0.0171	− 0.46	− 0.42	− 3.95
	4	1.0563	+ .5803	+ .3635	− 9.81	− 9.55	− 6.22
	5	1.0234	− .5146	− .1487	+ 4.02	+ 3.97	+ 1.34
	6	1.0351	+ .5899	+ .3782	−10.21	−10.04	− 8.83
benzyl	2	1.0	.5477	.2843	− 7.69		− 5.10
	3	1.0	− .5022	− .1482	+ 4.01		+ 1.60
	4	1.0	.5190	.2631	− 7.11		− 6.30
	7	1.0	.8090	.5922	−16.00		−16.40

is needed in (i) above. Use of (ii) does not significantly change these conclusions. The agreement with experiment is also satisfactory, for butadiene anion [13], although the coupling constant for position 2 is again too small.

For these molecules, the value of $\langle S^2 \rangle_{\mathrm{ASA}}$ is almost exactly $\frac{3}{4}$, its 'pure doublet' value; the further small spin impurities are presumably unimportant. However, for pentadienyl, benzyl and azulene anion, $\langle S^2 \rangle_{\mathrm{ASA}}$ is significantly greater than $\frac{3}{4}$. Also, the calculated coupling constants for pentadienyl [11] are in poor agreement with experiment, the relative orders of magnitude being incorrect, and the coupling constants for azulene anion [14] are completely wrong, even regarding orders of magnitude. This may be due to the effect of the spin impurities. For the benzyl radical, most calculations predict that $|a_2| > |a_4|$ whereas the converse is true experimentally. Apart from this point, our calculation gives excellent agreement with experiment. However, due to the large value $\langle S^2 \rangle_{\mathrm{ASA}}$, and the large change produced in the spin density by the effect of the annihilation of the quartet, this agreement must be regarded as being somewhat fortuitous.

Triplets

Again, the value $\omega = 1.4$ was used throughout this section. On the simple HMO picture, the normalised spin density in a conjugated alternant triplet is the same as in its mononegative and monopositive ions. Our results in Tab. 3 show that this is roughly true using our method. To interpret our results, we have used rela-

Table 3. *Triplets studied (same comments as for Tab. 2)*

Molecule	Atom	$(\varrho_{ii})_{\mathrm{SD}}$	$(\varrho_{ii})_{\mathrm{ASA}}$	a_i	a_{exp}
naphthalene*	1	+.5193	+.4609	− 6.21	−5.61
	2	+.0875	+.0875	− 1.21	−2.29
butadiene*	1	+.8524	+.8524	−11.50	–
	2	+.1476	+.1476	− 1.99	–

tion (i) above. (All the excess charges are, of course, zero.) The results for naphthalene triplet are in good agreement with experiment [16], with the same reservation as for the mononegative ion results, and we have also predicted the coupling constants for the lowest π triplet state of butadiene.

σ-*Radicals*

The 'Extended Hückel' method for describing σ electrons is well known [17, 18]. To compute the elements of the Hamiltonian matrices, we have used POPLE's [17] version, with off diagonal matrix elements taken as $-10\ S_{ij}$ eV, where S_{ij} is the overlap integral between orbitals χ_i and χ_j. These were computed using a program due to HOFFMAN [19], using the same molecular geometries as in other work [22].

There is no reason why ω should have the value 1.4 for σ radicals; indeed, it should vary for different types of orbitals [20]. However, for the present, we have used $(\omega\beta_0) = -3.4$ eV, although our results could presumably be improved by varying this quantity. The coupling constants of Tab. 4 were calculated using the relation $a_i = A\varrho_{ii}$ where $A = 876$ gauss, the theoretical value for a hydrogen 1*s* Slater orbital with exponent $\zeta = 1.2$.

The calculated proton hyperfine coupling constant for formyl is in good agreement with the experimental value of 137 gauss [11]. The value for ethynyl is in less good agreement, [21] but is still acceptable, especially when one considers that the proton spin density is very small. However, the calculated values for the vinyl radical are in the wrong relative order of magnitude [11], although the proton labelled 2 has the largest coupling constant of the three. In all cases the value $\langle S^2\rangle_{\mathrm{ASA}}$ is almost exactly $\frac{3}{4}$. The agreement with experiment could be improved by varying the parameters, although this was not done, in the present work.

Table 4. *σ radicals studied*

Molecule	Proton	P_{ii}	$(\varrho_{ii})_{\mathrm{SD}}$	$(\varrho_{ii})_{\mathrm{ASA}}$	a_i	a_{exp}
ethynyl	1	0.8743	−.0043	.0065	5.69	16.1
formyl	1	0.9754	.0939	.1051	92.07	137.0
vinyl	1	0.9677	−.0251	.0299	26.19	16.0
	2	0.9725	.1545	.1253	109.76	68.0
	3	0.9908	.0219	.0181	15.86	34.0

4. Conclusions

We have described a simple method for calculating spin density distributions in σ and π radicals, ions and triplets: the results are in reasonable agreement with experiment, provided that the effect of contamination from different spin multiplet functions is small. Projection of the required spin multiplet would presumably improve the agreement with experiment, in those cases.

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