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Unrestricted Hartree Fock Wave Functions and Hyperfine Coupling Constants in Aromatic Radicals

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It is shown that a simple expression, differing from the one currently used, must be adopted when calculating π electron spin densities from unrestricted H.F. wave functions in connection with the prediction of proton hyperfine couplings in aromatic free radicals. The proposed formula gives results which are almost identical to those one obtains after complete projection of the unwanted parts of the unrestricted function.

Es wird gezeigt, daß sich bei der Berechnung von π-Elektronen-Spindichten mit Hilfe uneingeschränkter Hartree-Fock-Funktionen im Zusammenhang mit der Vorhersage von Protonen-Hyperfeinkopplungskonstanten in aromatischen Radikalen ein einfacher, von dem häufig verwandten abweichender Ausdruck ergibt. Die vorgeschlagene Formel führt zu Ergebnissen, die fast mit denen identisch sind, die man nach vollständiger Projektion der unerwünschten Anteile der uneingeschränkten Funktion erhält.

Une expression simple, différant de celle couramment admise, est adopté pour le calcul des densités de spin π-électronique par les fonctions H.F. non-restreintes, afin de prédire les couplages hyperfins protoniques dans les radicaux benzéniques. Les résultats sont presqu'identiques à ceux de l'élimination, par projection, des parties à spin faux de la fonction non-restreinte.

Unrestricted Hartree Fock wave functions for π-electron systems are currently used to calculate π-electron spin densities for correlation with experimental proton hyperfine coupling constants of aromatic radicals, as obtained from ESR spectra, through the McCONNELL relationships [3]

$$a_H = Q\, \varrho_k \tag{1}$$

where a_H is the h.f.c.c. of the proton, ϱ_k the π-spin density on the attached carbon atom and Q a constant independent on the particular aromatic system.

Equation (1) is valid within certain approximations which do not include the one that the wave function may not be a correct spin eigenfunction. UHF w.f.'s are in fact not at all aigenfunctions of the S^2 operator.

The question has often been raised in the literature as to the validity of the use of UHF w.f.'s and as to the necessity of projecting out the doublet part of the wave function for calculating π-spin densities.

MARSHALL [5] shows that the unprojected functions give spin densities which are correct to first order "provided certain exchange energies are small relative to promotion energies".

On the other hand SNYDER and AMOS [6] find that annihilation of quartet and upper multiplicity components improve the agreement of the calculated spin densities with the experimental proton couplings.

In this note we show that, if one analyzes the form which the McCONNELL relationship (1) assumes for unrestricted single determinant wave functions, it is very easy to see that almost exactly the same results are obtained if one uses eq. (1), either

a) with a single determinant unrestricted wave function but using a corrected "ϱ" which is extremely easily obtained, or

b) with a completely projected wave function and the usual definition of ϱ.

Theory

We start by recalling how the McCONNELL relationship arises when the π-system is described by a restricted single determinant wave function of the type

$$\Psi_R^0 = |\, \sigma_k\, \overline{\sigma}_k\, \pi_1\, \overline{\pi}_1\, \pi_2\, \overline{\pi}_2 \ldots\ldots \pi_n\, \overline{\pi}_n\, \pi_0 \,| \tag{2}$$

where the σ orbital of the kth C-H bond under consideration is explicitly indicated [*3*, *4*].

$\sigma - \pi$ interaction mixes the excited state configuration

$$\Psi'_R = 1/\sqrt{6}\, [2\, |\, \sigma_k\, \sigma_k{}^*\, \pi_1\, \overline{\pi}_1 \ldots \pi_n\, \overline{\pi}_n\, \overline{\pi}_0 \,| - |\, \sigma_k\, \overline{\sigma}_k{}^*\, \pi_1\, \overline{\pi}_1 \ldots \pi_n\, \overline{\pi}_n\, \pi_0 \,| - \\ - |\, \overline{\sigma}_k\, \sigma_k{}^*\, \pi_1\, \overline{\pi}_1 \ldots \pi_n\, \overline{\pi}_n\, \pi_0 \,|]$$

with the ground state and, at first order, the spin density at the proton nucleus becomes proportional (through a constant depending only on the form and energy of the σ orbitals), to the matrix element

$$(H_{0,1})_R \equiv \langle\, \Psi_R^0 \,|\, H \,|\, \Psi'_R \rangle = -3/\sqrt{6}\, \langle\, \sigma_k^*\, \pi_0 \,|\, \frac{e^2}{r_{12}} \,|\, \pi_0\, \sigma_k \,\rangle\, .$$

Expanding π_0 in terms of atomic orbitals χ_i and neglecting all integrals except the one involving only the carbon orbital attached to the proton (χ_k), one gets:

$$(H_{0,1})_R \cong -3/\sqrt{6}\, \langle\, \sigma_k^*\, \chi_k \,|\, \frac{e^2}{r_{12}} \,|\, \chi_k\, \sigma_k \,\rangle\, c_{0k}^2\, .$$

For a restricted single determinant wave function $c_{0k}^2 \equiv \varrho_k$, hence eq. (1) follows immediately.

Now, in the unrestricted H.F. scheme, the zero order wave function is

$$\Psi_U^0 = |\, \sigma_k\, \overline{\sigma}_k\, \pi_1\, \overline{\pi}'_1\, \pi_2\, \overline{\pi}'_2 \ldots\ldots \pi_n\, \overline{\pi}'_n\, \pi_0 \,|$$

where the orbitals π_i are different from the π'_i; within each of the two sets orthogonality is ensured but there is no orthogonality among members of the two different sets.

The problem is now as to which wave function of the type Ψ'_U has to be mixed with Ψ_U^0 to give rise to the non zero proton spin density. If we take Ψ'_U to be of the same form as Ψ'_R, we probably shall have an excited state wave function which is as much a correct doublet wave function as is Ψ_U^0. This procedure is of course almost arbitrary at this stage but it seems the most logical one.

We then write:

$$\Psi'_U = 1/\sqrt{6}\, [2\, |\, \sigma_k\, \sigma_k^*\, \pi_1\, \overline{\pi}'_1\, \pi_2\, \overline{\pi}'_2 \ldots \pi_n\, \overline{\pi}'_n\, \overline{\pi}_0 \,| - |\, \sigma_k\, \overline{\sigma}_k^*\, \pi_1\, \overline{\pi}'_1 \ldots \pi_n\, \overline{\pi}'_n\, \pi_0 \,| - \\ |\, -\overline{\sigma}_k\, \sigma_k^*\, \pi_1\, \overline{\pi}'_1 \ldots \pi_n\, \overline{\pi}'_n\, \pi_0 \,|\,]\, .$$

The matrix element is in this case

$$\begin{aligned}(H_{0,1})_U &= \langle \Psi_U^0 \mid H \mid \Psi_U' \rangle \\ &= -\frac{3}{\sqrt{6}} \langle \sigma_k \pi_0 \mid \frac{e^2}{r_{12}} \mid \sigma_k^* \pi_0 \rangle + \frac{1}{\sqrt{6}} \sum_i \langle \sigma_k \pi_i' \mid \frac{e^2}{r_{12}} \mid \sigma_k^* \pi_i' \rangle - \\ &\quad - \frac{1}{\sqrt{6}} \sum_i \langle \sigma_k \pi_i \mid \frac{e^2}{r_{12}} \mid \sigma_k^* \pi_i \rangle + \frac{2}{\sqrt{6}} \sum_i \langle \sigma_k \pi_i' \mid \frac{e^2}{r_{12}} \mid \pi_0 \sigma_k^* \rangle S_{\pi_i' \pi_0}\end{aligned}$$

where $S_{\pi_i' \pi_0}$ is the overlap integral between the two orbitals π_i' and π_0.

If we now retain only integrals over the k carbon orbital, when expanding π_i as $\sum_j C_{ij} \chi_j$ and π_i' as $\sum_j C_{ij}' \chi_j$, we obtain:

$$\begin{aligned}(H_{0,1})_U = &-3/\sqrt{6} \langle \sigma_k^* \chi_k \mid \frac{e^2}{r_{12}} \mid \sigma_k \chi_k \rangle \left[C_{0k}^2 + \tfrac{1}{3} \sum_{i=1}^{n} (C_{ik}^2 - C_{ik}'^2) - \right. \\ &\left. - \tfrac{2}{3} \sum_{i=1}^{n} C_{0k} C_{ik}' S_{\pi_0 \pi_i'}\right] + \dots\dots\dots .\end{aligned}$$

The expression within square brackets is quite different from what is defined for ϱ_k for an unrestricted single determinant wave function, which is:

$$\varrho_k = C_{0k}^2 + \sum_{i=1}^{n} (C_{ik}^2 - C_{ik}'^2) . \tag{3}$$

If we adopt the above expression for $(H_{0,1})_U$, the McConnell relationship should read for unrestricted single determinant wave functions

$$a_H = Q \text{ ``}\varrho_k\text{''} \tag{4}$$

with

$$\text{``}\varrho_k\text{''} = C_{0k}^2 + \sum_{i=1}^{n} \left[\tfrac{1}{3} (C_{ik}^2 - C_{ik}'^2) - \tfrac{2}{3} C_{0k} C_{ik}' S_{\pi_0 \pi_i'}\right] . \tag{5}$$

Now, it has been shown by Marshall [5] that, neglecting small terms, the expression for ϱ one gets after complete projection of a wave function of type (2) made up with "corresponding" orbitals is

$$\varrho_k = C_{0k}^2 + \sum_{i=1}^{n} \tfrac{1}{3} (C_{ik}^2 - C_{ik}'^2) .$$

This is exactly the result expressed by (5) if we observe that for "corresponding" orbitals the term containing $S_{\pi_0 \pi_i'}$ is small because the primed and unprimed sets of "corresponding" orbitals are as much as possible orthogonal to each other.

It seems therefore justified to use eq. (5) in conjunction with McConnell's relationships to predict proton hyperfine couplings of aromatic radicals from unrestricted HF wave functions.

Application to Benzyl radical

The case of Benzyl radical is quite suitable to illustrate the correctness of eq. (5).

Benzyl is in fact an odd alternant radical, so that the unrestricted procedure is necessary to bring out the negative density at the meta position and furthermore no neighbour or charge corrections [4] are needed to estimate coupling constants and eq. (2) can be tested directly.

Baudet and Berthier [2] calculated unrestricted wave functions for this radical using a semiempirical procedure and computed spin densities both directly and after partially projecting out the unwanted multiplicities by a formula given by Amos and Hall [*1*].

They came to the conclusion that the results given by the direct calculation were closer to experiment when used in connection with eq. (1). The table shows their direct and partially projected results and the result one obtains with eq. (5).

Table. *Ring protons coupling constants and URHF spin densities for Benzyl radical*

Pos.	a_H (*Oe*) exp	ϱ			$Q = \frac{a_{H(\mathrm{exp})}}{\varrho}$		
		(1)	(2)	(3)	(1)	(2)	(3)
o	4.90	.238	.200	.173	20.6	24.5	28.3
m	1.50	−.133	−.089	−.045	11.3	16.8	33.3
p	6.10	.249	.207	.206	24.5	29.5	29.6

(1) Obtained from eq. (3).
(2) Obtained after a partial projection.
(3) Obtained from eq. (5).

It is quite obvious that eq. (5) gives the best results. They give a much better correlation for the small negative spin density at the meta position and improve also the *o*-, *p*-ratio of the coupling constants.

It is to be noted that in the wave functions used, the orbitals are not of the corresponding type so that the overlap term in eq. (5) is significant.

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Literature

[*1*] Amos, A. T., and G. G. Hall: Proc. Roy. Soc. **A 263**, 483 (1961).
[*2*] Baudet, J., and G. Berthier: J. Chim. physique **60**, 1161 (1963).
[*3*] McConnell, H., and D. B. Chesnut: J. chem. Physics **28**, 107 (1958).
[*4*] Giacometti, G., P. L. Nordio und M. V. Pavan: Theoret. chim. Acta (Berlin) **1**, 404 (1963).
[*5*] Marshall, W.: Proc. phys. Soc. **78**, 113 (1961).
[*6*] Snyder, L. G., and A. T. Amos: J. chem. Physics (in press).

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