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# Open Shell SCF MO CI Calculation of Spin Density Distributions

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Self Consistent Field Molecular Orbitals (SCF-MO's) computed using the method described by Roothaan [3] were used as basis functions in a calculation of the spin density distributions of a number of (open shell) $\pi$ electron anions and radicals. Electronic correlation was introduced into the ground state wavefunction by allowing it to interact with all singly excited configurations of the type $\frac{1}{\sqrt{6}}\left\{2\,|a\,x\,\bar{n}| - |a\,\bar{x}\,n| - |\bar{a}\,x\,n|\right\}$. The results agree well with experiment, and the method was applied without difficulty to some open shell heterocyclic anions.

Unter Benutzung einer Basis von SCF-Molekülfunktionen, die nach der Methode von Roothaan [3] erhalten wurden, sind die Spindichteverteilungen einer Reihe von $\pi$-Elektronen Anionen und Radikalen mit offenen Schalen berechnet worden. Die Wechselwirkung der Elektronen wurde durch eine CI-Rechnung unter Berücksichtigung aller einfach angeregten Zustände vom Typ $\frac{1}{\sqrt{6}}\left\{2\,|a\,x\,\bar{n}| - |a\,\bar{x}\,n| - |\bar{a}\,x\,\mathrm{n}|\right\}$ in die Funktion des Grundzustandes eingeführt. Die Resultate stimmen gut mit den Experimenten überein. Die Methode ließ sich ohne Schwierigkeit auf einige heterozyklische Anionen mit offener Schale anwenden.

En employant une base d'orbitales moléculaires au champ autocohérent (SCF-MO's) calculées d'après Roothaan [3], nous avons calculé les distributions de la densité de spin pour un nombre d'anions et de radicaux $\pi$-électroniques à couches ouvertes. Une corrélation électronique est introduite dans la fonction de l'état fondamental en le faisant interagir avec toutes les configurations monoexcitées dy typ $\frac{1}{\sqrt{6}}\left\{2\,|a\,x\,\bar{n}| - |a\,\bar{x}\,n| - |\bar{a}\,x\,n|\right\}$. Les résultats s'accordent bien à l'experience, et la méthode s'appliquait sans difficulté à quelques anions hétérocycliques à couches ouvertes.

## 1. Introduction

Many calculations of the electronic spectra of closed shell unsaturated organic molecules using the semi empirical SCF MO methods due to Pariser andParr [1], and Pople [2], have been reported, and generally show good agreement with experiment. However, open shell molecules such as benzyl and naphthalene anion have not been so extensively studied theoretically, the lack of results presumably being due to the greater complexity of the SCF problem.

An SCF treatment of open shell molecules has been given by Roothaan [3], and has been modified for $\pi$ electron systems, using the "zero differential overlap" approximation, by Adams and Lykos [4].

In a closed shell system, the SCF ground configuration does not interact with singly excited configurations (Brillouin's theorem) [5], but still interacts with doubly (and higher) excited configurations [*6*]. A SCF open shell ground configuration $| a \bar{a} \ldots m m n |$, can interact with singly excited states of the form

$$\Psi' (a, x) = \frac{1}{\sqrt{6}} \left\{ 2 \, | a \, x \, \bar{n} | - | a \, \bar{x} \, n | - | \bar{a} \, x \, n | \right\}$$

where $a$, $m$, $n$ and $x$ are molecular orbitals having occupation numbers 2, 2, 1, 0 respectively. For this reason, configurations of this type are referred to as pseudo doubly excited configurations, and are clearly important in spin density calculations, especially at positions where the spin density is small or zero, in the unperturbed ground state [*9*].

The open shell SCF method just described was used recently [*7, 8*] to compute basis orbitals for some aromatic anions, and hence unperturbed spin densities by squaring the coefficients of the singly occupied orbital. In one case, however [*8*], a new value of the energy of an electron in the localized atomic $2p\pi$ orbital centered on the nitrogen atoms, had to be used. No configuration interaction was included in this calculation, whilst HOIJTINK [*9*] calculated the spin density distribution in pyrene anion using a limited configuration interaction calculation treatment, and Hückel one-electron MO's as basis functions. Good agreement with the observed coupling constants was reported.

We have calculated the spin density distributions of a number of (doublet) conjugated radicals and anions, using open shell SCF MO's as basis functions in a configuration interaction calculation. The molecules studied are shown in the figure. We find that those parameter sets which give good agreement between experimental and predicted electronic spectra of some of the open shell molecules studied, also give a good description of their spin density distributions [*10, 11*].

## 2. Method and Parameters

The SCF MO's were obtained using the method described by ADAMS and LYKOS [*4*]. Hückel orbitals were used as "starting orbitals" in the SCF procedure, and in the cases of the nitrogen heterocyclics, and of phenoxyl, the values $h = 0.5$, 1.0 and $k = 0.8$, 0.8 as given by STREITWIESER [*12*] were used to generate the Hückel orbitals: this procedure greatly decreased the time taken for convergence, fifteen cycles generally being necessary to give seven figure consistency in the eigenvectors.

A first order pertubation treatment was then used to improve the SCF ground state, by admixture of singly excited configurations of the type $\Psi' (a, x)$, the basis set of configurations consisting of the ground state, together with all possible singly excited states of this form. The first order perturbation approach was considered adequate, since the contributions of the singly excited states to the ground state was never greater than 10%. The matrix elements needed in the calculation were obtained in the usual way [*13*]. The atomic one center coulomb integrals for carbon and nitrogen were 11.4 and 12.8 eV respectively. The value of $\delta\omega_N$ was $-1.68$ eV, as proposed by PEACOCK and McWEENY [*33*], whilst the values of the other integrals, and the methods of calculation have been given elsewhere [*11*].

The calculation of spin densities proceeded in the usual manner [*9*], and to check the calculation, the sum of spin densities was computed. In all cases, the total spin density was 1.0000.* The SCF bond order matrix, without configuration interaction, was also computed. All the molecules were assumed to have regular geometries: all bond lengths were taken 1.40 Å and all angles 120°, except for azulene, where symmetrical seven and five-membered rings were assumed.

## 3. Results and Discussion

The computed hydrogen hyperfine splittings were correlated with the experimental results, giving $Q_H = -27$ gauss. Thus, following Amos and Snyder [*14*], we have calculated the hydrogen hyperfine splitting constants using two relations

$$a_H = -27\,\varrho_i \tag{1}$$

$$a_H = -27\,\varrho_i - 12.8\,\varepsilon_i\,\varrho_i \tag{2}$$

where $\varepsilon_i = 1 - P_i$, $P_i$ being the usual charge density at position $i$. Nitrogen hyperfine splittings were also fitted to a similar relation, $a_N = -21\,\varrho_N$ giving the best fit. The best value of $Q_H$ for the hydrogen hyperfine splittings in the heterocyclic molecules was found to be $-26$ gauss.

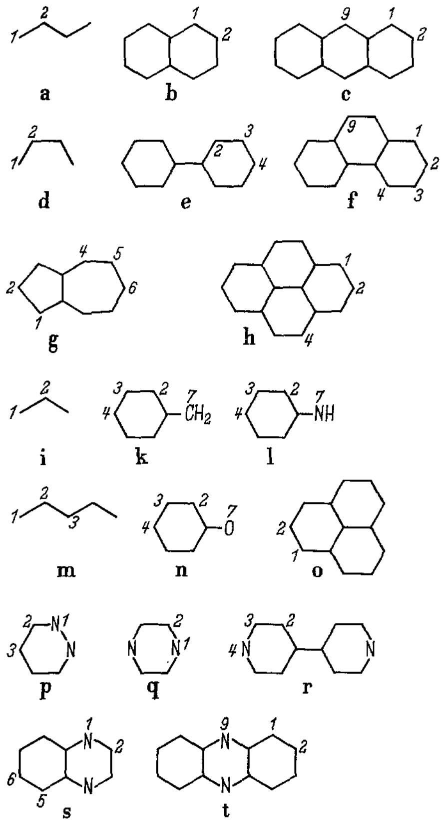

Fig. 1. Conjugated molecules studied. a) butadiene (trans); b) naphthalene; c) Anthracene; d) butadiene (cis); e) biphenyl; f) phenanthrene; g) azulene; h) pyrene; i) allyl; k) benzyl; l) anilino; m) pentadienyl; n) phenoxyl; o) perinaphthanyl; p) pyridazine; q) pyrazine; r) 4.4′ bipyridyl; s) phthalazine; t) phenazine

A recent calculation [*15*] of the relative spin densities in azulene anion and cation using closed shell SCF MO's as basis functions in a configuration interaction calculation showed good agreement with experiment and with other calculations for the anion, whilst for the cation, there was severe disagreement with the results obtained using an empirical valence bond approach [*16*]. As seen from Tab. 1, our results for azulene anion agree well, both with experiment and with Bloor's calculation [*15*] whereas the results for azulene cation again agree well with Bloor's but disagree with the valence bond calculation. Unfortunately, no experimental results are available for azulene cation despite the recent work on positive ion E.S.R. spectra [*17*].

The isoconjugate series benzyl, anilino and phenoxyl generally give poor agreement with those experimental results which are known; a summary of the results is given in Tab. 2. More specifically, the ortho/para ratio of splittings in benzyl and

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* For the calculation of the total spin density the data for certain carbon atoms "$i$" are needed, that are not given in the tables. We follow to the rule that calculated quantities, that can never hope to be observed, are not recorded. The point is that, if no $H$ is attached to carbon atom "$i$", no spin coupling effects will result.

Table 1. *Spin density distribution in the azulene anion and cation (in brackets). All coupling constants are in Gauss*

| | Spin Densities | | | Coupling Constants | | |
|---|---|---|---|---|---|---|
| | BLOOR [*15*] | BROWN [*16*] | Our | (a) | (b) | Expt. [*23*] |
| 1 | −.0238<br>(.4880) | .1300<br>(.2101) | −.0110<br>(.3738) | + 0.297 | +0.273 | +0.274 |
| 2 | .1064<br>(−.0773) | .1464<br>(−.0113) | .0854<br>(−.0902) | − 2.306 | −2.152 | −3.948 |
| 4 | .2396<br>(−.1209) | .3060<br>(.3333) | .2222<br>(−.0112) | − 6.000 | −5.907 | −6.219 |
| 5 | −.0690<br>(−.0478) | −.1585<br>(−.1855) | −.0505<br>(.0945) | + 1.364 | +1.330 | +1.338 |
| 6 | .3617<br>(−.0518) | .3513<br>(.3740) | .3722<br>(−.0222) | −10.049 | −9.200 | −8.829 |

phenoxyl is inverted, whilst our calculation generally agrees with other calculations [*18*] on these molecules. The high value (0.8) of the spin density on the methylene group of benzyl is almost certainly due to our choice of parameter sets. However, we have used those parameter sets which gave good agreement between the calculated and observed electronic spectra of these radicals [*11*], and it is perhaps surprising that such poor agreement with experiment should result.

The results for the even alternant hydrocarbon anions are presented in Tab. 3. These have been the subject of many theoretical investigations [*19*]. Simple Hückel theory gives satisfactory answers, provided that the MO containing the unpaired electron does not have a node at the position of a proton. The unrestricted Hartree-Fock perturbation method due to McLACHLAN [*20*] also gives good agreement with experiment, which is a little surprising, since the wavefunction is neither self consistent nor an eigenfunction of $S^2$.

Our calculations give good agreement, although some small positive and negative coupling constants calculated using both formulae 1 and 2, are generally overestimated. However, the *order* of magnitudes is always correct. The excess charge effect is certainly important in these cases, and relation (2) is probably more correct. To calculate $\varepsilon_i$, we have used the charge densities calculated before the introduction of configuration interaction into the ground state; again, since the contribution from singly excited states $\Psi'$ $(a, x)$ is usually less than 10%, this procedure is quite adequate. As the SCF bonding orbitals of the anions pair with

Table 2. *Spin density distribution in the series benzyl, anilino and phenoxyl*

| | Benzyl | | | Anilino | | Phenoxyl | | |
|---|---|---|---|---|---|---|---|---|
| Position | $\varrho$ | $a_{(a)}$ | $a_{(\exp)}$ [*24*] | $\varrho$ | $a_{(a)}$ | $\varrho$ | $a_{(a)}$ | $a_{(\exp)}$ [*24*] |
| 7 | .8040 | −21.71 | −16.40 | .7945 | | .6900 | | |
| 2 | .1248 | − 3.37 | − 5.10 | .1310 | −3.54 | .1819 | −4.91 | − 6.9 |
| 3 | −.0319 | + 0.86 | + 1.60 | −.0319 | +0.86 | −.0420 | +1.13 | (+) 1.9 |
| 4 | .0863 | − 2.33 | − 6.30 | .0873 | −2.36 | .1182 | −3.19 | − 10.1 |

Table 3. *Spin density distributions in some even alternant hydrocarbon anions*

| Anion | Position | Density | $a_{(a)}$ | $a_{(b)}$ | $a_{(\mathrm{exp})}$ |
|---|---|---|---|---|---|
| cis-butadiene [*25*] | 1 | .4035 | −10.89 | −8.80 | −7.62 |
| | 2 | .0965 | − 2.61 | −2.48 | −2.79 |
| trans butadiene [*25*] | 1 | .3815 | −10.30 | −8.50 | −7.62 |
| | 2 | .1185 | − 3.20 | −3.00 | −2.79 |
| naphthalene [*26*] | 1 | .2229 | − 6.02 | −5.49 | −4.90 |
| | 2 | .0474 | − 1.28 | −1.22 | −1.83 |
| anthracene [*27*] | 1 | .1068 | − 2.88 | −2.76 | −2.74 |
| | 2 | .0312 | − 0.85 | −0.80 | −1.57 |
| | 4 | .2734 | − 7.38 | −6.62 | −5.56 |
| biphenyl [*26*] | 2 | .1005 | − 2.71 | −2.60 | −2.75 |
| | 3 | −.0112 | + 0.30 | +0.29 | +0.45 |
| | 4 | .1699 | − 4.59 | −4.17 | −5.50 |
| phenanthrene [*28*] | 1 | .1278 | − 3.45 | −3.26 | −3.60 |
| | 2 | −.0241 | + 0.65 | +0.64 | +0.72 |
| | 3 | .0992 | − 2.68 | −2.50 | −2.88 |
| | 4 | .0366 | − 0.79 | −0.97 | −0.32 |
| | 9 | .2227 | − 6.01 | −5.50 | −4.32 |
| pyrene [*9*] | 1 | .1646 | − 4.44 | −4.11 | −4.75 |
| | 2 | −.0395 | + 1.07 | +1.06 | +1.09 |
| | 4 | .0948 | − 2.56 | −2.44 | −2.08 |

the (virtual) SCF antibonding orbitals of the cations, then it is expected that both cation and anion should have the same spin density distributions. For this reason, we have not calculated the spin densities of the even alternant hydrocarbon cations. However, as the excess charges will be different in anion and cation, so will the coupling constants, calculated by relation (2).

Hoijtink [*21*] et al. first examined the electronic spectra of the anions of many alternant hydrocarbons and was able to explain the experimental results quite well, using simplified CI treatments. It has been shown recently [*10*] that better agreement results using SCF procedures to calculate the electronic spectra, and it is probably both significant and important that both the E.S.R. and $\pi$-electronic spectra can be explained well by the same method and the same set of parameters.

Table 4. *Spin density distribution in some odd alternant hydrocarbon radicals*

| Radical | Position | $\varrho$ | $a_{(a)}$ | $a_{(\mathrm{exp})}$ |
|---|---|---|---|---|
| allyl [*29*] | 1 | 0.5616 | −15.16 | −14.38 |
| | 2 | −.1232 | + 3.33 | + 4.06 |
| pentadienyl [*29*] | 1 | +.3300 | − 8.91 | − 8.99 |
| | 2 | −.0915 | + 2.47 | + 2.65 |
| | 3 | +.5232 | −14.13 | −13.40 |
| perinaphthanyl [*30*] | 1 | .2149 | −11.20 | − 7.30 |
| | 2 | −.0530 | + 1.43 | + 2.20 |

Table 5. *Spin density distributions in some N-heterocyclic alternant even anions; coupling constants calculated using $Q_H = -27$ gauss; $Q_N = -21$ gauss*

| | Position | No C. I. | C. I. | (Mucci) [*8*] | Calc. a | exp. a |
|---|---|---|---|---|---|---|
| pyrazine [*31*] | 1 | .3357 | .3789 | .249 | −7.96 | −7.21 |
| | 2 | .0821 | .0605 | .126 | −1.63 | −2.64 |
| pyridazine [*32*] | 1 | .2451 | .2797 | .283 | −5.87 | −5.90 |
| | 2 | .0003 | −.0638 | .018 | +1.72 | (+)0.16 |
| | 3 | .2547 | .2842 | .199 | −7.67 | −6.47 |
| 4,4′ bipyridyl [*33*] | 2 | | .1007 | | −2.72 | −2.35 |
| | 3 | | −.0058 | | +0.16 | (+)0.43 |
| | 4 | | .1504 | | −3.16 | −3.64 |
| phthalazine [*33*] | 1 | | .1986 | | −4.17 | −5.64 |
| | 2 | | .0449 | | −1.21 | −3.32 |
| | 5 | | .2331 | | −6.29 | −2.32 |
| | 6 | | .0653 | | −1.76 | −1.00 |
| phenazine [*33*] | 1 | .0871 | .1054 | .066 | −2.85 | −1.93 |
| | 2 | .0370 | .0333 | .038 | −0.90 | −1.61 |
| | 9 | .2229 | .2627 | .198 | −5.52 | −5.14 |

The results for the odd alternant radicals, apart from benzyl, anilino and phenoxyl, all appear in Tab. 4. Good agreement with experiment results, although again the coupling constants of small modulus are overestimated in the prediction. There is no excess charge in the radicals (a consequence of the pairing theorem [*22*]), and so we have only used expression (1) to calculate the coupling constants. The antibonding orbitals pair with the bonding orbitals in the usual way.

The results for the nitrogen heterocyclics, together with those given by Mucci et al. [*8*] are presented in Tab. 5. The values reported by Mucci were obtained using $\delta\omega_N = -4.79$ eV, and for comparison, we have presented our results without configuration interaction. It is probable that Mucci's value for $\delta\omega_N$ is necessitated by the neglect of configuration interaction, which can alter the spin distribution quite drastically. Our values including configuration interaction agree well with experiment, using the relations $a_H = -26\,\varrho_C$; $a_N = -21\varrho_N$.

## 4. Conclusions

Whilst many empirical and semi-empirical calculations of spin densities have been made, the correctness of a wavefunction must be ascertained by results it gives for *all* physical observables. To this end, previous calculations [*10*, *11*] on $\pi$-electronic spectra of open shell molecules, have given reasonable explanations of two physical observables using the same wavefunctions, SCF methods and parameter sets.

The influence of doubly excited states on the spin densities is probably much smaller than that of singly excited states; whilst such calculations are possible, at present the real problem would appear to be the correlation between the experimental result (coupling constant) and the calculated result (spin density).

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