Perturbation Calculation of Spin Densities in π-Electron Radicals

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The unrestricted Hartree-Fock perturbation technique was applied to the calculation of spin densities in many hydrocarbon radicals. The method is similar to that of McLachlan but contains partly the SCF and projection procedures. The results agree with the more rigorous SCF ones.

Spin density distributions in conjugated radicals and ions can be successfully explained by the simplified unrestricted McLachlan method.[1)] Though approximate UHF functions without projection are used, the spin densities thus obtained are in good agreement with experiment. A discussion on this has been given by Snyder and Amos.[2)] They concluded that this might be caused by compensating errors, the use of a single SCF iteration and the failure to project or annihilate. The McLachlan method does not appear to be theoretically well founded. Modified versions of the method have been presented by many authors[3)–8)] without due attention to theory.

This paper presents an alternative form of the McLachlan method within the perturbed Hückel approximation. Since our approach still contains the SCF and projection procedures, the spin densities in π-electron radicals and ions calculated can be compared with the results obtained by the more rigorous UHF method.

Theory

Let us consider a doublet ground state for a conjugated radical. According to Brickstock and Pople[9)] the SCF π-electron Hamiltonian matrix elements are given by

$$\left.\begin{aligned} F^{\alpha(\beta)}_{\mu\mu} &= U_{\mu\mu} + P^{\beta(\alpha)}_{\mu\mu}\gamma_{\mu\mu} + \sum_{\nu\neq\mu}(P_{\nu\nu}-Z_\nu)\gamma_{\mu\nu} \\ F^{\alpha(\beta)}_{\mu\nu} &= \beta_{\mu\nu} - P^{\alpha(\beta)}_{\mu\nu}\gamma_{\mu\nu} \qquad\qquad (\mu\neq\nu) \end{aligned}\right\} \tag{1}$$

where

$$P^{\alpha(\beta)}_{\mu\nu} = \sum_{i}^{\text{occ.}} C^{\alpha(\beta)}_{i\mu} C^{\alpha(\beta)}_{i\nu}$$

$$P_{\mu\nu} = P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}$$

and the superscripts α and β refer to α and β electrons respectively. Throughout this paper, Greek suffixes will be used for atomic orbitals and italics for molecular orbitals. Let us take the arithmetical mean values of the matrix elements given by Eq. 1 as

$$\left.\begin{aligned} \bar{F}_{\mu\mu} &= \frac{1}{2}(F^{\alpha}_{\mu\mu}+F^{\beta}_{\mu\mu}) = U_{\mu\mu} + \frac{1}{2}P_{\mu\mu}\gamma_{\mu\mu} \\ &\quad + \sum_{\nu\neq\mu}(P_{\nu\nu}-Z_\nu)\gamma_{\mu\nu} \\ \bar{F}_{\mu\nu} &= \frac{1}{2}(F^{\alpha}_{\mu\nu}+F^{\beta}_{\mu\nu}) = \beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu} \\ &\qquad\qquad (\mu\neq\nu). \end{aligned}\right\} \tag{2}$$

These matrix elements are just those defined by Longuet-Higgins and Pople.[10)] From Eqs. 1 and 2 we obtain

$$\left.\begin{aligned} \Delta F^{\alpha}_{\mu\nu} &= F^{\alpha}_{\mu\nu} - \bar{F}_{\mu\nu} = -\frac{1}{2}\rho_{\mu\nu}\gamma_{\mu\nu} \\ \Delta F^{\beta}_{\mu\nu} &= F^{\beta}_{\mu\nu} - \bar{F}_{\mu\nu} = \frac{1}{2}\rho_{\mu\nu}\gamma_{\mu\nu} \end{aligned}\right\} \tag{3}$$

where

$$\rho_{\mu\nu} = P^{\alpha}_{\mu\nu} - P^{\beta}_{\mu\nu}. \tag{4}$$

Equation 3 suggests that the approximate restricted Hartree-Fock method of Longuet-Higgins and Pople[10)] is a good starting point for perturbation treatment of the UHF method.

We are now in a position to formulate the spin density by means of perturbation theory. Equation 4 is modified as

$$\begin{aligned} \rho_{\mu\nu} &= (\overline{P^{\alpha}_{\mu\nu}}-\overline{P^{\beta}_{\mu\nu}}) + (\Delta P^{\alpha}_{\mu\nu}-\Delta P^{\beta}_{\mu\nu}) \\ &= \rho^{\circ}_{\mu\nu} + (\Delta P^{\alpha}_{\mu\nu}-\Delta P^{\beta}_{\mu\nu}) \end{aligned} \tag{5}$$

where

$$\overline{P^{\alpha}_{\mu\nu}} - \overline{P^{\beta}_{\mu\nu}} = C_{0\mu}C_{0\nu} = \rho^{\circ}_{\mu\nu}$$

$$\Delta P^{\alpha(\beta)}_{\mu\nu} = P^{\alpha(\beta)}_{\mu\nu} - \overline{P^{\alpha(\beta)}_{\mu\nu}}$$

$\overline{P^{\alpha(\beta)}_{\mu\nu}}$ and $\rho^{\circ}_{\mu\nu}$ stand for the corresponding quantities of $P^{\alpha(\beta)}_{\mu\nu}$ and $\rho_{\mu\nu}$, respectively, within the RHF scheme. We can put

$$\Delta P^{\alpha(\beta)}_{\mu\nu} = \sum_{\kappa\lambda}\Pi^{\alpha(\beta)}_{\mu\nu,\kappa\lambda}\Delta F^{\alpha(\beta)}_{\kappa\lambda} \tag{6}$$

where the polarizability $\Pi^{\alpha(\beta)}_{\mu\nu,\kappa\lambda}$ can be defined as

$$\Pi^{\alpha(\beta)}_{\mu\nu,\kappa\lambda} = \partial\overline{P^{\alpha(\beta)}_{\mu\nu}}/\partial\bar{F}_{\kappa\lambda}.$$

Since

$$\overline{P^{\alpha}_{\mu\nu}} + \overline{P^{\beta}_{\mu\nu}} = \overline{P_{\mu\nu}}$$

we obtain

$$\partial\overline{P_{\mu\nu}}/\partial\overline{F_{\kappa\lambda}} = \Pi^{\alpha}_{\mu\nu,\kappa\lambda} + \Pi^{\beta}_{\mu\nu,\kappa\lambda} \equiv \Pi_{\mu\nu,\kappa\lambda}. \tag{7}$$

Using Eqs. 3, 6, and 7, the resulting expression for the spin density matrix elements is reduced to

$$\rho_{\mu\nu} = \rho^{\circ}_{\mu\nu} - \frac{1}{2}\sum\Pi_{\mu\nu,\kappa\lambda}\rho_{\kappa\lambda}\gamma_{\kappa\lambda}. \tag{8}$$

If we restrict ourselves to the consideration of atom spin densities only, Eq. 8 becomes

$$\rho_{\mu\mu} = \rho^{\circ}_{\mu\mu} - \frac{1}{2}\sum_{\nu}\Pi_{\mu\mu,\nu\nu}\rho_{\nu\nu}\gamma_{\nu\nu}. \tag{9}$$

Since Hückel-type and SCF-type MO's do not differ significantly, according to McLachlan,[1)] the Hückel-type MO's can be applied introducing a parameter λ. Thus Eq. 9 can be written as

$$\rho_{\mu\mu} = \rho^{\circ}_{\mu\mu} - \lambda\sum_{\nu}\Pi_{\mu\nu}\rho_{\nu\nu} \tag{10}$$

where the $\Pi_{\mu\nu}$ are dimensionless atom-atom polarizabilities. From Eq. 7, they are defined by

$$\Pi_{\mu\nu} = 4\sum_{i}^{\substack{\text{doubly}\\\text{occ.}}}\sum_{j\neq i}^{\text{all}}\frac{C_{i\mu}C_{j\mu}C_{i\nu}C_{j\nu}}{\varepsilon_i-\varepsilon_j} + 2\sum_{k\neq 0}^{\text{all}}\frac{C_{0\mu}C_{k\mu}C_{0\nu}C_{k\nu}}{\varepsilon_0-\varepsilon_k} \tag{11}$$

or

$$\Pi_{\mu\nu} = \Pi_{\mu\nu}^{(0)} + \Pi_{\mu\nu}^{(1)} \tag{12}$$

where

$$\left.\begin{aligned} \Pi_{\mu\nu}^{(0)} &= 4 \sum_{i}^{\substack{\text{doubly}\\ \text{occ.}}} \sum_{j}^{\text{vac.}} \frac{C_{i\mu}C_{j\mu}C_{i\nu}C_{j\nu}}{\varepsilon_i - \varepsilon_j} \\ \Pi_{\mu\nu}^{(1)} &= \sum_{i}^{\substack{\text{doubly}\\ \text{occ.}}} \frac{C_{i\mu}C_{0\mu}C_{i\nu}C_{0\nu}}{\varepsilon_i - \varepsilon_0} + 2\sum_{j}^{\text{vac.}} \frac{C_{0\mu}C_{j\mu}C_{0\nu}C_{j\nu}}{\varepsilon_0 - \varepsilon_j}. \end{aligned}\right\} \tag{13}$$

Subscript 0 refers to the odd electron orbital. The polarizability defined by Eq. 11 or 12 is not that for closed shell molecules but is valid for radicals and ions. A similar definition of polarizability has also been proposed by Devolder,8) but it was incorrect.7) It is easy to show that the pairing theorem holds for alternant hydrocarbons, even if the polarizability defined above is used in our theory; that is, the spin density distributions in the anion and cation of an even alternant are expected to be identical.

Equation 10 is similar to the McLachlan formula,1) but is in principle a simultaneous equation. The explicit solution of Eq. 10 can be written as

$$\rho_{\mu\mu}^{\text{UHF}} = \sum_{\nu} X_{\mu\nu} \rho_{\nu\nu}^{\circ} \tag{14}$$

where

$$X_{\mu\nu} = (-1)^{\mu+\nu} \Delta_{\mu\nu}/\Delta$$

$$\Delta = \det\{\delta_{\mu\nu} + \lambda\Pi_{\mu\nu}\}.$$

$\Delta_{\mu\nu}$ is the determinant obtained by striking out the μth column and νth row from the determinant Δ. The equation can be rewritten as

$$\rho_{\mu\mu}^{\text{UHF}} = \rho_{\mu\mu}^{\circ} - \lambda \sum \Pi_{\mu\nu}^{\text{SCF}} \rho_{\nu\nu}^{\circ} \tag{15}$$

where

$$\Pi_{\mu\nu}^{\text{SCF}} = (\delta_{\mu\nu} - X_{\mu\nu})/\lambda. \tag{16}$$

The $\rho_{\mu\mu}^{\text{UHF}}$ thus obtained approximately corresponds to the spin density for the SCF UHF function, though a perturbation theory is used in our approach where the SCF procedure is partly introduced by solving the simultaneous equation instead of iterations. Such an SCF perturbation theory was applied successfully to the bond order problem by Coulson and Golebiewski.11) Validity of the procedure is confirmed by the numerical results.

In general, UHF spin densities do not agree with experiment because of spin contamination. Let us now introduce the projection procedure to our approach. To the first order of perturbation theory, the spin density for the projected UHF function is given by

$$\rho_{\mu\mu}^{\text{PUHF}} = \rho_{\mu\mu}^{\circ} - \frac{1}{3}\lambda \sum_{\nu} \Pi_{\mu\nu}^{(0)} \rho_{\nu\nu}^{\circ} - \lambda \sum_{\nu} \Pi_{\mu\nu}^{(1)} \rho_{\nu\nu}^{\circ} \tag{17}$$

where the last term comes from the pure doublet configurations, so it is left through a projection.2,12—15) However, within the SCF perturbation theory, such a procedure as separating the last two terms of Eq. 17 may be cumbersome; our aim is to obtain a simplified formula. Fortunately, Snyder and Amos2) suggested that the following approximation is practically reasonable.

$$\rho_{\mu\mu}^{\text{PUHF}} \approx \rho_{\mu\mu}^{\circ} - \frac{1}{3}\lambda \sum_{\nu} \Pi_{\mu\nu}^{\text{SCF}} \rho_{\nu\nu}^{\circ} \tag{18}$$

Therefore we may approximate the projected spin density as above.

Let us deal with the next difinition of spin density. If the $\rho_{\nu\nu}$ which appears in the second term of Eq. 10 can be approximated as the $\rho_{\nu\nu}^{\circ}$, we have

$$\rho_{\mu\mu}^{\text{MMc}} = \rho_{\mu\mu}^{\circ} - \lambda \sum_{\nu} \Pi_{\mu\nu} \rho_{\nu\nu}^{\circ}. \tag{19}$$

The approximation indicates the use of the usual perturbation theory instead of the SCF one. Equation 19 is now formally reduced to the McLachlan formula.1) However, our formula is different from McLachlan's in the definition of polarizabilities, which is given by Eq. 11 or 12.

Calculations and Results

First let us evaluate the adjustable parameter λ. McLachlan obtained $\lambda = \gamma/2|\beta| \approx 1.2$ using the parameter of Pariser and Parr $\gamma = 10.53$ eV. However, Gutfreund and Little16) concluded from the consideration of the screened potential that the γ values are of the order of 7—9 eV in most cases for large π-electron systems, depending on the position of the given atomic site in the molecule. To a cruder approximation, we can neglect the small variation of β and position dependence of γ, taking the average value of γ. The λ values then become proportional to the constant γ. It can be inferred that the average value of γ for the anion is smaller than for the corresponding cation and the neutral radical falls into the middle, since the γ values can be considered to be proportional to the screening constants. On this assumption, the spin density distributions for the anion and the corresponding cation differ from each other, indicating a violation of the pairing theorem. However, the pairing theorem should be valid only within certain approximations; a more rigorous theory violates it. For instance, a renouncement of the approximations of zero-differential overlap or an introduction of penetration energies into the term $U_{\mu\mu}$ which appears in Eq. 1 or 2 leads to breakdown of the pairing theorem. Our assumption is thus reasonable.

On the other hand, the experimental fact that the proton hyperfine splittings of the anions and the corresponding cations of even alternants are not identical has so far been accounted for by using the Colpa-Bolton (CB) relationship17) which includes the charge effect or the Giacometti-Nordio-Pavan (GNP) effect18) including that of the nearest-neighbor bond spin densities. However, both relations fail to explain the fact that the lower splittings (for example, at the 2 position of anthracene and naphthacene in Tables 1 and 2) for cations are generally smaller in magnitude than for the corresponding anions in contrast to what is found for the higher splititngs.

In view of the discussion above we will introduce partly the small difference between cations and the corresponding anions into our theory by adjusting the parameter λ. Let us take the λ values as $\lambda = 1.1$, 1.0, and 0.9 for cations, neutral radicals and anions, respec-

TABLE 1. PROTON HYPERFINE SPLITTINGS FOR THE ANIONS AND CATIONS OF ANTHRACENE AND NAPHTHACENE (G)[a,b]

Radical	Atom[c]	M[d]				CB[e]				GNP[f]				Expt.[g]
		PUHF	MMc	SA (aa)	Mc	PUHF	MMc	SA (aa)	Mc	PUHF	MMc	SA (aa)	Mc	
Anthracene$^{\mp}$	1	−2.78 −2.86	−2.91 −2.97	−2.83	−3.18	−2.65 −3.00	−2.77 −3.12	−2.72 −2.97	−3.04 −3.33	−2.52 −3.12	−2.66 −3.23	−2.65 −3.03	−2.93 −3.44	−2.76 −3.12
	2	−1.11 −1.02	−1.00 −0.92	−0.75	−0.86	−1.08 −1.05	−0.98 −0.94	−0.73 −0.80	−0.84 −0.88	−0.97 −1.17	−0.85 −1.08	−0.65 −0.87	−0.74 −0.99	−1.53 −1.40
	9	−6.07 −6.48	−6.59 −6.89	−7.02	−6.91	−5.48 −7.13	−5.90 −7.63	−6.32 −7.74	−6.28 −7.54	−5.57 −6.98	−6.10 −7.38	−6.40 −7.64	−6.41 −7.42	−5.41 −6.65
Naphthacene$^{\mp}$	1	−1.59 −1.65	−1.62 −1.65	−1.49	−1.76	−1.55 −1.69	−1.58 −1.69	−1.46 −1.53	−1.71 −1.80	−1.49 −1.75	−1.52 −1.75	−1.33 −1.65	−1.65 −1.86	−1.55 −1.72
	2	−0.76 −0.70	−0.68 −0.62	−0.43	−0.62	−0.74 −0.71	−0.66 −0.63	−0.42 −0.45	−0.61 −0.64	−0.70 −0.76	−0.62 −0.67	−0.35 −0.51	−0.56 −0.68	−1.15 −1.06
	5	−4.56 −4.83	−4.99 −5.21	−5.32	−5.10	−4.21 −5.22	−4.59 −5.65	−4.91 −5.73	−4.75 −5.46	−4.28 −5.12	−4.71 −5.50	−4.81 −5.83	−4.83 −5.37	−4.25 −5.17

a) Where pairs of members are given, the upper value is for the anion and the lower for the cation. b) Each notation refers to the corresponding spin density listed in Table 2. c) For the numbering see Ref. 2. d) Calculated using the McConnell relationship with the numerical coefficient in Ref. 2. e) Calculated using the CB relationship[16] with the numerical coefficients in Ref. 2. f) Calculated using the GNP relationship[17] with the numerical coefficients in Ref. 2. The bond spin densities are defined in a similar manner to the atomic ones. g) Sources listed in Ref. 2.

tively. The test calculation is carried out for the cations and anions of anthracene and naphthacene. The proton hyperfine splittings and the spin densities calculated are given in Tables 1 and 2, respectively. We see that our calculation gives better agreement with experiment than the others. It should especially be noted that our calculation predicts the relative magnitudes of splittings at the 2 positions of the cations and anions except for the GNP relationship, though the magnitudes are too low. This seems to support our assumption. We will therefore employ the values above throughout this paper.

Secondly, let us see whether the $\rho_{\mu\mu}^{UHF}$ values defined by Eq. 14 or 15 coincide with the spin densities obtained by means of the more elaborate UHF method. The values of $\rho_{\mu\mu}^{UHF}$ for a number of hydrocarbon radicals and ions are computed and compared with the spin densities (before annihilation) obtained by Snyder and Amos[2] (Table 2). The spin densities agree reasonably well with each other except for some positions of benzil. This seems to justify our SCF perturbation treatment. Moreover, if it is borne in mind that the perturbed Hückel MO's are used in our treatment, and the SCF MO's in theirs, it may be regarded as an unexpected success.

We have computed the spin densities $\rho_{\mu\mu}^{PUHF}$ and $\rho_{\mu\mu}^{MMc}$ defined by Eqs. 18 and 19 respectively, for a number of hydrocarbon radicals and ions in order to compare the results with the ones obtained by Snyder and Amos[2] and by McLachlan[1] (Table 2). A close inspection of Table 2 shows the following :

1) As a whole the values of the four different expressions of spin densities $\rho_{\mu\mu}^{PUHF}$, $\rho_{\mu\mu}^{MMc}$, ρ_{aa}^{SA}, and ρ^{Mc} agree fairly well with each other.

2) In particular agreement between $\rho_{\mu\mu}^{MMc}$ and ρ^{Mc}, and between $\rho_{\mu\mu}^{PUHF}$ and ρ_{aa}^{SA} is quantitatively good.

3) The values of $\rho_{\mu\mu}^{PUHF}$ and $\rho_{\mu\mu}^{MMc}$ are in good agreement with each other in spite of different difinitions.

The discrepancy between the $\rho_{\mu\mu}^{MMc}$ and ρ^{Mc} spin densities is due to the use of different values of λ and $\Pi_{\mu\nu}$ except for odd alternant hydrocarbon radicals. A similar discussion applies to a comparison of the $\rho_{\mu\mu}^{PUHF}$ and ρ_{aa}^{SA} values.

Let us now compare the $\rho_{\mu\mu}^{PUHF}$ and $\rho_{\mu\mu}^{MMc}$ spin densities. The important difference between the two is that the projected UHF functions and the SCF perturbation theory are used for the former, and unprojected ones and a simple perturbation theory for the latter. Nevertheless the two give almost equivalent spin densities. This seems to give numerical evidence of the validity of the McLachlan-type formulas. The theoretical basis of the formulas is not yet established, but agreement between them may probably be due to accidental cancellation in errors when a perturbation method is used. The problem has been discussed by Snyder and Amos.[2]

Discussion

Our theory employs the perturbed Hückel approach with use of the SCF and projection procedures. The McLachlan-type formulas are therefore obtained as a special case. We wish to clarify the correlation between the McLachlan-type formulas and ours.

Since $\lambda \approx 1$ and usually $|\Pi_{\mu\nu}| < 1$, we may expand the SCF polarizability $\Pi_{\mu\nu}^{SCF}$ as

$$\Pi_{\mu\nu}^{SCF} = \Pi_{\mu\nu} - \lambda \sum_{\kappa} \Pi_{\nu\kappa}\Pi_{\kappa\nu} + \cdots \tag{20}$$

Substituting Eq. 20 into Eq. 15, we obtain

$$\rho_{\mu\mu}^{UHF} = \rho^{\circ}_{\mu\mu} - \lambda \sum_{\nu} \Pi_{\mu\nu}\rho^{\circ}_{\nu\nu} + \lambda^2 \sum_{\nu\kappa} \Pi_{\mu\kappa}\Pi_{\kappa\nu}\rho^{\circ}_{\nu\nu} + \cdots \tag{21}$$

By comparing Eq. 21 with Eq. 19 we see that the difference between the UHF spin density $\rho_{\mu\mu}^{UHF}$ and the modified McLachlan-type one $\rho_{\mu\mu}^{MMc}$ is the quadratic and higher order terms of polarizabilities. The contributions from these higher order terms to the spin density appear to be rather small. However, the order of magnitude of the $\Pi_{\mu\nu}$ $(\Pi_{\mu\mu}+\Pi_{\nu\nu})$ which appears in the second term of Eq. 20 can be compared with the one of the first term $\Pi_{\mu\nu}$. Actually the order

TABLE 2. SPIN DENSITIES CALCULATED WITH VARIOUS METHODS FOR ALTERNANT AND NON-ALTERNANT HYDROCARBON RADICALS AND IONS[a)]

Radical	Atom	This work			Work of Snyder and Amos		Work of McLachlan
		$\rho^{\mathrm{UHF}}_{\mu}$	$\rho^{\mathrm{PUHF}}_{\mu\mu}$	$\rho^{\mathrm{MMc}}_{\mu\mu}$	$\rho^{\mathrm{SA}}_{\mathrm{sd}}$ b)	$\rho^{\mathrm{SA}}_{\mathrm{aa}}$ c)	ρ^{Mc}
Ally	1	0.688	0.563	0.588	0.651	0.547	0.588
	2	−0.376	−0.126	−0.177	−0.302	−0.093	−0.177
Benzyl	1	−0.238	−0.079	−0.102	−0.189	−0.060	−0.102
	2	0.225	0.170	0.161	0.254	0.157	0.161
	3	−0.149	−0.050	−0.063	−0.158	−0.050	−0.063
	4	0.140	0.142	0.137	0.225	0·128	0.137
	7	0.947	0.697	0.770	0.771	0.718	0.770
Butadiene$^-$	1	0.466	0.397	0.416	0.457	0.389	0.442
	2	0.034	0.103	0.084	0.043	0.111	0.058
Naphthalene$^-$	1	0.233	0.200	0.213	0.262	0.215	0.222
	2	0.042	0.059	0.054	0.026	0.048	0.047
	9	−0.050	−0.019	−0.033	−0.076	−0.024	−0.037
Anthracene$^{\mp}$	1	0.117 0.126	0.103 0.106	0.108 0.110	0.138	0.105	0.118
	2	0.027 0.018	0.041 0.038	0.037 0.034	0.014	0.028	0.032
	9	0.289 0.334	0.225 0.240	0.244 0.255	0.319	0.260	0.256
	11	−0.029 −0.050	−0.007 −0.014	−0.017 −0.022	−0.061	−0.014	−0.028
Naphthacene$^{\mp}$	1	0.065 0.071	0.059 0.061	0.060 0.061	0.078	0.055	0.065
	2	0.018 0.012	0.028 0.026	0.025 0.023	0.006	0.016	0.023
	5	0.213 0.243	0.169 0.179	0.185 0.193	0.252	0.197	0.189
	13	−0.018 −0.030	0.002 −0.002	−0.005 −0.009	−0.041	−0.005	−0.010
	17	−0.065 −0.086	−0.019 −0.026	−0.029 −0.036	−0.088	−0.028	−0.033
Azulene$^-$	1	0.008	0.005	−0.019	−0.011	−0.001	−0.027
	2	0.099	0.100	0.111	0.118	0.080	0.120
	4	0.367	0.269	0.276	0.313	0.236	0.292
	5	−0.185	−0.055	−0.058	−0.178	−0.046	−0.081
	6	0.403	0.308	0.327	0.434	0.356	0.368
	9	0.060	0.077	0.082	0.099	0.093	0.071
Fluoranthene$^-$	1	0.200	0.148	0.149	0.189	0.140	0.157
	2	−0.082	−0.013	−0.014	−0.102	−0.020	−0.023
	3	0.279	0.202	0.212	0.304	0.228	0.227
	7	−0.006	0.009	0.004	−0.024	−0.003	0.000
	8	0.036	0.038	0.037	0.041	0.029	0.037
	11	−0.089	−0.030	−0.035	−0.130	−0.041	−0.039
	12	0.015	0.005	−0.012	0.026	0.012	−0.013
	13	0.046	0.067	0.074	0.051	0.070	0.063
	14	0.064	0.061	0.061	0.089	0.070	0.064
Acenaphthylene$^-$	1	0.102	0.103	0.106	0.111	0.097	0.101
	3	0.250	0.184	0.188	0.216	0.158	0.196
	4	−0.115	−0.029	−0.033	−0.123	−0.029	−0.041
	5	0.300	0.219	0.228	0.317	0.236	0.245
	9	−0.101	−0.034	−0.040	−0.138	−0.044	−0.045
	10	0.022	0.007	−0.011	0.050	0.017	−0.012
	11	0.002	0.036	0.036	0.023	0.052	0.027

a) See footnotes a) and c) in Table 1. b) Before annihilation. c) After annihilation.

of magnitude of $\Pi^{SCF}_{\mu\nu}$ is fairly greater than the one of $\Pi_{\mu\nu}$ in many cases. Our result confirms this; the $\rho^{MMc}_{\mu\mu}$ spin density is far from the $\rho^{UHF}_{\mu\mu}$ one at many positions of radicals (Table 2). In the following we will discuss the question why such a crude model as the McLachlan method can successfully interpret experimental results.

Marshall[12)] showed that the unprojected spin density should be closer to experimental result than the projected one under certain conditions. On the other hand, Snyder and Amos[2)] showed that in first order to Lowdin's extended Hartree-Fock scheme,[19)] in terms of our theory, the spin density can be approximated as[20)]

$$\rho^{EXT}_{\mu\mu} \approx \rho^{\circ}_{\mu\mu} - K\lambda \sum_{\nu} \Pi^{SCF}_{\mu\nu} \rho^{\circ}_{\nu\nu} \tag{22}$$

where K is a dimensionless coefficient which can be expressed as some ratio of energy terms; if $K=1$ the $\rho^{EXT}_{\mu\mu}$ is reduced to the $\rho^{UHF}_{\mu\mu}$ and if $K=1/3$ to the $\rho^{PUHF}_{\mu\mu}$. Most radicals fall between these extremes, the conjugated hydrocarbon radicals appearing to approximate the second case. They suggested that the McLachlan spin density, which falls between the unprojected UHF spin densities and projected ones in most cases, can be good approximations to the ones obtained by the extended Hartree-Fock method. Our results also confirm the suggestion; since $|\Pi_{\mu\nu}| \lesssim |\Pi^{SCF}_{\mu\nu}|$ in many cases, if $K \lesssim 1$ the $\rho^{MMc}_{\mu\mu}$ might agree with the $\rho^{EXT}_{\mu\mu}$. This condition is practically satisfied together with that $K \gtrsim 1/3$ in most cases. Harriman and Sando[21)] demonstrated explicitly that this is true in many cases by their numerical results, though K is rather closer to unity.

A comparison is given between our approach and that given in other works. Recently Amos *et al.*[22)] suggested a method for improving the spin densities obtained from UHF wave functions. Their procedure differs from ours; they have employed the usual perturbation theory, while we take the self-consistency effect into consideration. Nakatsuji and Hirao[23)] have proposed a pseudo-orbital theory which corresponds to an extension of UHF and spin-extended HF theories, containing self-consistency terms.

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