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Some Remarks on the Calculations of Hyperfine Splittings in the ESR Spectra of Conjugated Radicals*

JAN WASILEWSKI and WIESŁAW WOŹNICKI
Institute of Physics, Nicholas Copernicus University, Grudziądzka 5, Toruń, Poland

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Some consequences of non-orthogonality of the basic functions of LCAO approximation, on the relations used for calculations of hyperfine splittings in ESR spectra of conjugated radicals, are discussed. Special attention has been paid on the problem of transferability of the hyperfine coupling constants. The discussion is illustrated by some calculations of the hyperfine splittings for radical-ions of naphthalene, and tetracene.

Einige Folgerungen aus der Nichtorthogonalität der Basis in der LCAO-Näherung für die Beziehungen, die für die Berechnung der Hyperfeinaufspaltung im ESR-Spektrum konjugierter Radikale benutzt werden, werden untersucht. Insbesondere wird die Frage der Übertragbarkeit der Hyperfeinkopplungskonstanten behandelt. Die Diskussion wird durch einige Berechnungen der Hyperfeinaufspaltung für die Radikalionen des Naphtalins und des Tetracens ergänzt.

It is well known that the isotropic hyperfine structure of ESR spectra of conjugated hydrocarbon radicals is due to the Fermi contact interaction between unpaired electron spin and the nuclear spins of protons adjacent to the conjugated carbon atoms. According to McConnell [1], the hyperfine splitting a_{H_α}, generated by the interaction of electron spin with the spin of a proton bonded to the carbon atom α, can be in a rough approximation expressed as

$$a_{\mathrm{H}_\alpha} = \text{constant} \times [\phi_{(\mathrm{CH})_\alpha} \varphi_0 \,|\, \varphi_0 \phi_{(\mathrm{CH})_\alpha^*}] \,. \tag{1}$$

In the molecular exchange integral written above, $\phi_{(\mathrm{CH})_\alpha}$ and $\phi_{(\mathrm{CH})_\alpha^*}$ are the bonding and antibonding localized orbitals, respectively, of the $\mathrm{C}_\alpha - \mathrm{H}$ bond under consideration, φ_0 is the singly occupied π-electronic molecular orbital. After introducing the LCAO approximation

$$\varphi_0 = \boldsymbol{\chi} \boldsymbol{C}_0 = \sum_{\mu} \chi_\mu C_{\mu 0} \,,$$

we obtain the relation (1) in the following matrix form:

$$a_{\mathrm{H}_\alpha} = \mathrm{Tr}(\boldsymbol{G}^{\mathrm{H}_\alpha} \boldsymbol{Q}) \,. \tag{2}$$

$\boldsymbol{G}^{\mathrm{H}_\alpha}$ is a matrix of hyperfine coupling constants, having the elements

$$G_{\mu\nu}^{\mathrm{H}_\alpha} = \text{constant} \times (\phi_{(\mathrm{CH})_\alpha} \chi_\mu \,|\, \chi_\nu \phi_{(\mathrm{CH})_\alpha^*}) \,. \tag{3}$$

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$\boldsymbol{Q}$ is the matrix representation of the spin density operator in the atomic orbital basis $\boldsymbol{\chi}$,

$$\boldsymbol{Q}=\boldsymbol{C}_0\boldsymbol{C}_0^+$$

(the ground state of the radical is well described by the single-determinantal wavefunction).

In semiempirical schemes there are several possibilities of approximations concerning the structure of the hyperfine coupling matrix $\boldsymbol{G}^{\mathrm{H}_\alpha}$. In the simplest case these matrices can be reduced to single elements, $G_{\alpha\alpha}^{\mathrm{H}_\alpha}\equiv G$ (for any α). This approximation will be further referred to as approximation I:

$$G_{\mu\nu}^{\mathrm{H}_\alpha(\mathrm{I})}=\begin{cases} G & \mu=\nu=\alpha\,, \\ 0 & \text{otherwise}\,. \end{cases} \tag{4}$$

Then the general formula (2) takes the form:

$$a_{\mathrm{H}_\alpha}^{(\mathrm{I})}=G\,Q_{\alpha\alpha}\,, \tag{5}$$

where the protonic coupling constant G can be treated as a transferable empirical parameter, characterizing some properties of C–H bond in conjugated radicals. The approximation I means that, among the integrals (3), only those of the type $(\phi_{(\mathrm{CH})_\alpha}\chi_\alpha|\chi_\alpha\phi_{(\mathrm{CH})_\alpha^*})$ have the values considerably different from zero. Therefore, in a better approximation we can assume a common non-zero value also for integrals of the type $(\phi_{(\mathrm{CH})_\alpha}\chi_\alpha|\chi_{\alpha_b}\phi_{(\mathrm{CH})_\alpha^*})$, where α_b designates any conjugated carbon atom bonded to the atom α. This approximation, referred to here as approximation II, can be written in the following way:

$$G_{\mu\nu}^{\mathrm{H}_\alpha(\mathrm{II})}=\begin{cases} G & \mu=\nu=\alpha\,, \\ g & \mu=\alpha,\ \nu=\alpha_b \quad \text{or} \quad \nu=\alpha,\ \mu=\alpha_b\,. \\ 0 & \text{otherwise}\,. \end{cases} \tag{6}$$

In this case we obtain from (2) the relation

$$a_{\mathrm{H}_\alpha}^{(\mathrm{II})}=G\,Q_{\alpha\alpha}+2g\,Q_{\alpha b} \tag{7}$$

$\left(\text{we introduce a shorthand notation } Q_{\alpha b}\equiv\sum_{(b)}Q_{\alpha\alpha_b}\right)$.

In semiempirical methods the eigenvalue problem determining molecular orbitals is practically always formulated in some orthogonalized basis, but not in the original (non-orthogonal) atomic orbital basis $\boldsymbol{\chi}$. The Löwdin-Orthogonalized Atomic Orbitals (LOAO) [2]

$$\boldsymbol{\lambda}=\boldsymbol{\chi}\boldsymbol{S}^{-\frac{1}{2}}, \quad \text{where} \quad S_{\mu\nu}=\langle\chi_\mu|\chi_\nu\rangle\,,$$

are most frequently (but often implicitly) used, especially in the PPP-type methods, e.g. [3]. Then, from the eigenvalue problem one obtains the eigenvectors ${}^{(\lambda)}\boldsymbol{C}_i$, connected with the original LCAO vectors $\boldsymbol{C}_i$ by the formula:

$${}^{(\lambda)}\boldsymbol{C}_i=\boldsymbol{S}^{\frac{1}{2}}\boldsymbol{C}_i\,,$$

and after that the spin density matrix in the $\boldsymbol{\lambda}$ basis is constructed as it follows:

$${}^{(\lambda)}\boldsymbol{Q}={}^{(\lambda)}\boldsymbol{C}_0\,{}^{(\lambda)}\boldsymbol{C}_0^+\,.$$

The general formula (2) can obviously be written in the equivalent form:

$$a_{\mathrm{H}_\alpha} = \mathrm{Tr}({}^{(\lambda)}\boldsymbol{G}^{\mathrm{H}_\alpha}\,{}^{(\lambda)}\boldsymbol{Q}), \tag{8}$$

where

$${}^{(\lambda)}\boldsymbol{Q} = \boldsymbol{S}^{\frac{1}{2}}\boldsymbol{Q}\boldsymbol{S}^{\frac{1}{2}}$$

and

$${}^{(\lambda)}\boldsymbol{G}^{\mathrm{H}_\alpha} = \boldsymbol{S}^{-\frac{1}{2}}\boldsymbol{G}^{\mathrm{H}_\alpha}\boldsymbol{S}^{-\frac{1}{2}}.$$

Usually, the hyperfine splittings are calculated from (8) by considering the matrix elements of ${}^{(\lambda)}\boldsymbol{Q}$ and making approximations either of the Type I (4) or II (6) on the matrices ${}^{(\lambda)}\boldsymbol{G}^{\mathrm{H}_\alpha}$, but not on $\boldsymbol{G}^{\mathrm{H}_\alpha}$. In this way one obtains the well known relation of McConnell (M) [1]

$$a_{\mathrm{H}_\alpha}^{\mathrm{M}} = {}^{(\lambda)}G\,{}^{(\lambda)}Q_{\alpha\alpha}, \tag{9}$$

and that of Giacometti, Nordio, and Pavan (GNP) [4]:

$$a_{\mathrm{H}_\alpha}^{\mathrm{GNP}} = {}^{(\lambda)}G\,{}^{(\lambda)}Q_{\alpha\alpha} + 2\,{}^{(\lambda)}g\,{}^{(\lambda)}Q_{\alpha b}. \tag{10}$$

It should be noted that the validity of the relations M (9) and GNP (10) is not justified by the same arguments as those leading from (2) either to (5) or to (7), because the "coupling constants" ${}^{(\lambda)}G$ and ${}^{(\lambda)}g$ are expressible by integrals of the type (3), but containing the multicenter orthogonalized orbitals $\boldsymbol{\lambda}$ instead of localized orbitals $\boldsymbol{\chi}$

$$(\text{e.g. } {}^{(\lambda)}G \equiv {}^{(\lambda)}G_{\alpha\alpha}^{\mathrm{H}_\alpha} \sim (\phi_{(\mathrm{CH})_\alpha}\lambda_\alpha | \lambda_\alpha \phi_{(\mathrm{CH})_\alpha^*})).$$

For these reasons the quantities ${}^{(\lambda)}G$ and ${}^{(\lambda)}g$ cannot be treated, in principle, as transferable empirical parameters. On the other hand, the relations M, and especially GNP, with transferable "coupling constants" are known as rather effective ones. This point will be further discussed in more detail.

It is well established experimentally that the total width of ESR spectrum is approximately constant for several classes of conjugated radicals, e.g. for radical-ions of poliacenes. This fact is in agreement with the M relation, since:

$$\mathrm{Tr}\,{}^{(\lambda)}\boldsymbol{Q} = 1.$$

Due to this equation the diagonal elements of ${}^{(\lambda)}\boldsymbol{Q}$ are usually called "spin densities on the conjugated atoms." This interpretation does not seem to be the most appropriate one, because the quantities defined in the basis $\boldsymbol{\lambda}$ cannot be treated as having the local properties. Moreover, it should be noticed that neither the diagonal elements of $\boldsymbol{Q}$ can be treated as the "spin densities", because in general

$$\mathrm{Tr}\,\boldsymbol{Q} \neq 1.$$

Some insight into the consequences of non-orthogonality of the atomic orbital basis $\boldsymbol{\chi}$ on the calculations of hyperfine splittings can be achieved in the following way. We can split the hyperfine coupling matrix into the diagonal part $\boldsymbol{G}_0^{\mathrm{H}_\alpha}$ and the off-diagonal one, $\boldsymbol{G}_1^{\mathrm{H}_\alpha}$:

$$\boldsymbol{G}^{\mathrm{H}_\alpha} = \boldsymbol{G}_0^{\mathrm{H}_\alpha} + \boldsymbol{G}_1^{\mathrm{H}_\alpha}, \tag{11}$$

where

$$G^{H_\alpha}_{0,\mu\nu} = G^{H_\alpha}_{\mu\nu}\,\delta_{\mu\nu}, \qquad G^{H_\alpha}_{1,\mu\nu} = G^{H_\alpha}_{\mu\nu}(1-\delta_{\mu\nu})\,;$$

analogously, we can do the same with the overlap matrix $\boldsymbol{S}$:

$$\boldsymbol{S} = \boldsymbol{1} + \boldsymbol{S}_1\,.$$

Let us introduce the following matrix:

$$\tilde{\boldsymbol{G}}^{H_\alpha} = \boldsymbol{G}^{H_\alpha}_1 - \tfrac{1}{2}\left(\boldsymbol{G}^{H_\alpha}_0 \boldsymbol{S}_1 + \boldsymbol{S}_1 \boldsymbol{G}^{H_\alpha}_0\right), \tag{12}$$

having the diagonal elements equal to zero and the off-diagonal ones of the form:

$$\tilde{G}^{H_\alpha}_{\mu\nu} = G^{H_\alpha}_{\mu\nu} - \tfrac{1}{2}\, S_{\mu\nu}\left(G^{H_\alpha}_{\mu\mu} + G^{H_\alpha}_{\nu\nu}\right). \tag{13}$$

One can easily show the identity

$$\begin{aligned} {}^{(\lambda)}\boldsymbol{G}^{H_\alpha} &= \tfrac{1}{2}\left(\boldsymbol{S}^{-\frac{1}{2}} \boldsymbol{G}^{H_\alpha}_0 \boldsymbol{S}^{\frac{1}{2}} + \boldsymbol{S}^{\frac{1}{2}} \boldsymbol{G}^{H_\alpha}_0 \boldsymbol{S}^{-\frac{1}{2}}\right) \\ &\quad + \boldsymbol{S}^{-\frac{1}{2}} \tilde{\boldsymbol{G}}^{H_\alpha} \boldsymbol{S}^{-\frac{1}{2}}\,. \end{aligned} \tag{14}$$

Substituting (14) into (8) we obtain

$$a_{H_\alpha} = \mathrm{Tr}\left(\boldsymbol{G}^{H_\alpha}_0 \boldsymbol{q}\right) + R_\alpha\,, \tag{15}$$

where

$$\begin{aligned} \boldsymbol{q} &= \tfrac{1}{2}\left(\boldsymbol{S}^{-\frac{1}{2}}\,{}^{(\lambda)}\boldsymbol{Q}\,\boldsymbol{S}^{\frac{1}{2}} + \boldsymbol{S}^{\frac{1}{2}}\,{}^{(\lambda)}\boldsymbol{Q}\,\boldsymbol{S}^{-\frac{1}{2}}\right) \\ &= \tfrac{1}{2}\left(\boldsymbol{Q}\boldsymbol{S} + \boldsymbol{S}\boldsymbol{Q}\right), \end{aligned} \tag{16}$$

and the “remainder” R_α can be written as follows:

$$R_\alpha = \mathrm{Tr}\left(\boldsymbol{S}^{-\frac{1}{2}} \tilde{\boldsymbol{G}}^{H_\alpha} \boldsymbol{S}^{-\frac{1}{2}}\,{}^{(\lambda)}\boldsymbol{Q}\right) = \mathrm{Tr}\left(\tilde{\boldsymbol{G}}^{H_\alpha} \boldsymbol{Q}\right). \tag{17}$$

If one wishes to preserve the concept of “spin densities on conjugated atoms” it seems that the diagonal elements of $\boldsymbol{q}$ (16) are the most convenient quantities for giving them such interpretations. Let us note that the definition (16) is analogous to Mulliken’s well-known definition of the atomic population [5], and that the matrix $\boldsymbol{q}$ has the correct trace:

$$\mathrm{Tr}\,\boldsymbol{q} = 1\,. \tag{18}$$

Moreover, when the approximations either I or II are introduced, (15) leads to

$$a^{(A)}_{H_\alpha} = G\,q_{\alpha\alpha} + R^{(A)}_\alpha \qquad (A = \mathrm{I}, \mathrm{II})\,. \tag{19}$$

Hence, if we have some arguments to consider $R^{(A)}_\alpha$ as a small quantity, we obtain the McConnell’s type relation with transferable coupling constants. In this case, due to (18), we are still in agreement with the above mentioned experimental fact of approximate constancy of the total width of the ESR pattern; it is also evident that $\sum_\alpha R_\alpha$ is responsible for deviations from this constancy.

Let us discuss the magnitude of the “remainder” $R^{(A)}_\alpha$ in more detail. When starting from the second part of (17), applying approximation I and neglecting the overlap integrals between non-nearest neighbours, we have

$$R^{(\mathrm{I})}_\alpha \cong -G\,S\,Q_{ab}\,, \tag{20}$$

where S is the average value of the overlap integrals between adjacent carbon atoms. Analogously, in approximation II we have

$$R_\alpha^{(\mathrm{II})} \cong 2(g - \tfrac{1}{2}\, GS)\, Q_{ab}\,. \tag{21}$$

The generally accepted estimations for the values of coupling constants, e.g. [4, 6] (referring, in principle, to the values of ${}^{(\lambda)}G$ and ${}^{(\lambda)}g$) indicate that the constants G and g are of the same sign, and the ratio G/g is in the range 5–6. Taking into account the average value of $S = 0.3$ we can estimate the term $-GS$ as a relatively large one, whereas the term $2(g - \frac{1}{2}\, GS)$ should be much smaller. It means that the quantity $G q_{\alpha\alpha}$ differs considerably from $a_{\mathrm{H}_\alpha}^{(\mathrm{I})} = G Q_{\alpha\alpha} = G q_{\alpha\alpha} + R_\alpha^{(\mathrm{I})}$, being at the same time quite close to $a_{\mathrm{H}_\alpha}^{(\mathrm{II})} = G Q_{\alpha\alpha} + 2g Q_{ab} = G q_{\alpha\alpha} + R_\alpha^{(\mathrm{II})}$. Therefore, we can expect the values of $G q_{\alpha\alpha}$ to interpret the experimental hyperfine splittings in a reasonable way, because approximation II seems to be physically better justified than approximation I.

On the other hand, the "remainder" R_α can be discussed formally in terms of the power series in $\boldsymbol{S}_1$ matrix, by using the expansion

$$R_\alpha = R_{\alpha,0} + R_{\alpha,1} + R_{\alpha,2} + \cdots .$$

Considering the presence of $\boldsymbol{S}_1$ in the definition (12) of $\tilde{\boldsymbol{G}}^{\mathrm{H}_\alpha}$, expanding $\boldsymbol{S}^{-\frac{1}{2}}$ in the usual way

$$\boldsymbol{S}^{-\frac{1}{2}} = \mathbf{1} - \tfrac{1}{2}\boldsymbol{S}_1 + \tfrac{3}{8}\boldsymbol{S}_1^2 - \cdots$$

and starting from the first part of (17), we obtain:

$$\begin{aligned} R_{\alpha,0} &= \mathrm{Tr}\,(\boldsymbol{G}_1^{\mathrm{H}_\alpha}\, {}^{(\lambda)}\boldsymbol{Q})\,, \\ R_{\alpha,1} &= -\mathrm{Tr}\,[\boldsymbol{S}_1(\boldsymbol{G}_0^{\mathrm{H}_\alpha} + \boldsymbol{G}_1^{\mathrm{H}_\alpha})\, {}^{(\lambda)}\boldsymbol{Q}]\,, \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{aligned}$$

Let us consider $R_{\alpha,0}$. The application of approximations either I or II gives, respectively:

$$\begin{aligned} R_{\alpha,0}^{(\mathrm{I})} &= 0\,, \\ R_{\alpha,0}^{(\mathrm{II})} &= 2g\, {}^{(\lambda)}Q_{ab}\,. \end{aligned} \tag{22}$$

It can be easily shown that ${}^{(\lambda)}\boldsymbol{Q}$ and $\boldsymbol{q}$ differ in terms of the order $\boldsymbol{S}_1^2$. Therefore, in the zeroth order of approximation we can write:

$$\begin{aligned} a_{\mathrm{H}_\alpha,0}^{(\mathrm{I})} &= G q_{\alpha\alpha} + R_{\alpha,0}^{(\mathrm{I})} \cong G\, {}^{(\lambda)}Q_{\alpha\alpha} \equiv a_{\mathrm{H}_\alpha}^{\mathrm{M}}\,, \\ a_{\mathrm{H}_\alpha,0}^{(\mathrm{II})} &= G q_{\alpha\alpha} + R_{\alpha,0}^{(\mathrm{II})} \cong G\, {}^{(\lambda)}Q_{\alpha\alpha} + 2g\, {}^{(\lambda)}Q_{ab} \equiv a_{\mathrm{H}_\alpha}^{\mathrm{GNP}}\,. \end{aligned} \tag{23}$$

In this way we have obtained the M and GNP relations with transferable coupling constants. However, the derivation (23) of both of the relations should be regarded with caution, for the terms of the first, or even of the second orders in $\boldsymbol{S}_1$ can be relatively large, and therefore $a_{\mathrm{H}_\alpha,0}^{(A)}$ can be a rather poor approximation to $a_{\mathrm{H}_\alpha}^{(A)}$ (with the same coupling constants used in both relations). In particular, as we have shown before, $G q_{\alpha\alpha} \cong G\, {}^{(\lambda)}Q_{\alpha\alpha}$ is significantly different from $a_{\mathrm{H}_\alpha}^{(\mathrm{I})}$ but it should be relatively close to $a_{\mathrm{H}_\alpha}^{(\mathrm{II})}$. Obviously, the M and GNP relations can be obtained directly from (8) by application of the power series expansions to ${}^{(\lambda)}\boldsymbol{G}^{\mathrm{H}_\alpha}$ and ${}^{(\lambda)}\boldsymbol{Q}$, but it seems to us that the way of reasoning presented here gives a slightly better insight into the structures of approximations involved in calculations of the hyperfine splittings.

In order to illustrate the discussion presented above, we have calculated the matrices $\boldsymbol{Q}$, ${}^{(\lambda)}\boldsymbol{Q}$, and $\boldsymbol{q}$, as well as the hyperfine splittings, for radical-ions of naphthalene, anthracene, and tetracene. All these results are collected in the Table 1. Molecular orbitals have been determined from the modified semi-empirical SCF LCAO method [7, 8], formulated in the way which takes fully into account the non-orthogonality of atomic orbital basis in the form of the Fock matrix. The details concerning the values of empirical parameters used are unimportant in our discussion except for the average values of overlap integrals between nearest neighbours, $S=0.333$; further details will be given elsewhere [9].

The important effect obtained as a result of the method applied here is a breaking of the well known pairing properties of molecular orbitals of anions and cations of the same alternant system, e.g. [10]. In particular, the diagonal matrix elements of ${}^{(\lambda)}\boldsymbol{Q}$ for anions and cations have different values on the corresponding positions (see the 5th column of the Table 1). Obviously, the similar effect can be observed for the corresponding elements of $\boldsymbol{Q}$ and $\boldsymbol{q}$ (see the columns: 3rd and 7th).

In order to calculate the hyperfine splittings, the values of coupling constants have been determined by minimalization of the standard error for the relation considered:

$$\sigma=\sqrt{\sum_{\alpha} p_\alpha (a_{\mathrm{H}_\alpha}^{\mathrm{calc.}}-\bar{a}_{\mathrm{H}_\alpha}^{\mathrm{exp.}})^2}\,. \tag{24}$$

The summation in (24) is extended on the set of all the 16 hyperfine splitting constants appearing in the ESR spectra of the systems investigated; $\bar{a}_{\mathrm{H}_\alpha}^{\mathrm{exp.}}$ is the arithmetic mean of the experimental values quoted in the columns 9–11 of the Table 1. The statistical weight p_α is proportional to the multiplicity of a given splitting in the ESR pattern of the system investigated, renormalized according to the condition $\sum_\alpha p_\alpha=1$.

At first, the validity of approximation I has been checked. The relation (5) with optimized value of coupling constant (in the manner described above) has the form

$$a_{\mathrm{H}_\alpha}^{(\mathrm{I})}=-24.36\,Q_{\alpha\alpha} \tag{25}$$

(all the coupling constants and hyperfine splittings are given in gausses). The calculated splittings are presented in the 12th column of the Table 1. We note that these values are rather in disagreement with the experimental ones, especially for the largest splitting; they lead therefore to a considerable value for the standard error. It is well-known from experiment that the largest splittings are larger in the ESR spectra of cation-radicals than the corresponding splittings in the anion-radicals spectra. Unfortunately, our approximation I leads to the opposite results. Therefore, we conclude that this approximation is too poor to describe the regularities observed in the spectra.

In the next step, the coupling constants G and g appearing in the relation (7) have been commonly optimized and we have obtained

$$a_{\mathrm{H}_\alpha}^{(\mathrm{II})}=-26.07\,Q_{\alpha\alpha}-10.40\,Q_{\alpha b}\,. \tag{26}$$

Table 1. The results of calculations for radical-ions of naphthalene, anthracene, and tetracene

Radical	Position	Elements of spin density matrices						Hyperfine splitting constants (all the values in gausses)						
		Q		$^{(\lambda)}Q$		q					Calculated (in brackets: standard error (24))			
	α	$Q_{\alpha\alpha}$	$Q_{\alpha b}$	$^{(\lambda)}Q_{\alpha\alpha}$	$^{(\lambda)}Q_{\alpha b}$	$q_{\alpha\alpha}$	$q_{\alpha b}$	Experimental			a (0.6451)	b (0.2240)	c (0.4091)	d (0.2562)
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
								[11]	[12, 13]	[14, 15]				
N^-	1	0.258	−0.155	0.187	−0.109	0.187	−0.108	−4.94	−4.95	−4.90	−6.28	−5.11	−4.88	−5.40
	2	0.093	−0.062	0.063	−0.046	0.063	−0.045	−1.825	−1.87	−1.83	−2.27	−1.78	−1.64	−1.83
								[14]	[14]	[15]				
N^+	1	0.177	0.099	0.187	0.109	0.187	0.109	−4.90	−5.20	−5.54	−4.31	−5.64	−4.88	−5.40
	2	0.055	0.044	0.063	0.045	0.063	0.046	−1.83	−1.78	−2.06	−1.34	−1.89	−1.64	−1.83
								[17]	[12]	[14, 15]				
A^-	1	0.131	−0.065	0.101	−0.043	0.100	−0.043	−2.726	−2.76	−2.74	−3.19	−2.74	−2.63	−2.83
	2	0.063	−0.028	0.047	−0.020	0.047	−0.022	−1.513	−1.53	−1.51	−1.53	−1.35	−1.23	−1.36
	9	0.248	−0.098	0.192	−0.072	0.193	−0.070	−5.346	−5.41	−5.56	−6.04	−5.45	−5.04	−5.57
								[17]	[16]	[14]				
A^+	1	0.093	0.036	0.091	0.035	0.091	0.035	−3.061	−3.08	−3.11	−2.27	−2.80	−2.37	−2.63
	2	0.039	0.021	0.041	0.020	0.041	0.020	−1.379	−1.38	−1.40	−0.95	−1.24	−1.07	−1.18
	9	0.226	0.076	0.220	0.082	0.222	0.082	−6.533	−6.49	−6.56	−5.50	−6.68	−5.80	−6.41
								[18]	[14]					
T^-	1	0.187	−0.055	0.147	−0.041	0.147	−0.041	−4.25	−4.25		−4.46	−4.20	−3.83	−4.24
	2	0.073	−0.022	0.059	−0.018	0.058	−0.018	−1.55	−1.49		−1.77	−1.67	−1.54	−1.67
	3	0.043	−0.013	0.033	−0.011	0.033	−0.011	−1.15	−1.17		−1.05	−0.99	−0.68	−0.95
								[19]	[14]					
T^+	1	0.176	0.011	0.164	0.044	0.166	0.044	−5.06	−5.17		−4.29	−4.70	−4.34	−4.79
	2	0.050	0.013	0.047	0.011	0.047	0.012	−1.69	−1.74		−1.22	−1.44	−1.23	−1.36
	3	0.025	0.011	0.026	0.009	0.026	0.009	−1.03	−1.03		−0.61	−0.77	−0.68	−0.75

a: relation (25), b: relation (26), c: relation (27), coupling constant G from (26), d: relation (27), optimized coupling constant.
N: naphthalene, A: anthracene, T: tetracene, +, − designate cation and anion, respectively.

The result for splitting constants are given in the 13th column of the Table 1. Now, the standard error is approximately three times smaller than in the former case. Moreover, the interpretation of all the splittings is quite satisfactory, in particular we observe the correct description of the largest splittings. Therefore, approximation II seems to be physically resonable and numerically effective. On the basis of the coupling constants optimized here we can estimate more precisely the constant values appearing in the formulas (20) and (21) for $R_\alpha^{(A)}$. They are: $-GS=8.69$, $2(g-\frac{1}{2}GS)=-1.71$; so our previous estimation of these terms was of correct order. We will treat the relation (26) as a starting point for further discussion.

For an additional check of our conclusions, the hyperfine splittings have also been calculated from the relation:

$$a_{\mathrm{H}_\alpha}=G q_{\alpha\alpha}\cong G\,{}^{(\lambda)}Q_{\alpha\alpha}\,, \tag{27}$$

using the optimized G value from our basic relation (26). As one should expect the interpretation of the splittings is, at least qualitatively, correct (see the 14th column of the Table 1). We can therefore conclude that (27) provides a fairly good approximation to (26). In particular, the regularities concerning the largest splittings in the radical-anions and -cations are preserved. This is due to the above mentioned fact of breaking of the pairing properties; namely, the largest spin densities $q_{\alpha\alpha}$ are in our calculations mostly larger for cations than for anions. This shows that the proper inclusion of the effects connected with the non-orthogonality of the atomic orbital basis into the method determining molecular orbitals [7, 8] is of importance in calculations of the spin densities. However, the calculated standard error is considerably greater than the corresponding value obtained in the case of the basic relation (26). This means that the "remainder" $R_\alpha^{(\mathrm{II})}$ is still non-negligible. It seemed interesting to us, to optimize separately the value of coupling constant appearing in (27). The optimum value is -28.87, the hyperfine splittings calculated from (27) with this G value can be found in the 15th column of the Table 1. The results are surprisingly good, but, of course, they are slightly worse than those obtained from (26). Undoubtedly, this optimized G value contains some contribution from the "remainder" R_α, and, therefore, transferability of the value obtained in this way is not quite clear. In any case our calculations show that the matrix $\boldsymbol{q}$ (or ${}^{(\lambda)}\boldsymbol{Q}$) can be used for reasonable interpretation of ESR spectra of conjugated radicals in the framework of the McConnell's type relation.

Finally, we conclude that the most appropriate way to obtain the correct description of the ESR spectra of the radicals is to employ the relation (7) based on our approximation II, which involves the matrix $\boldsymbol{Q}$, being a representation of the spin density operator in the basis of "true" atomic orbitals χ. This matrix can be easily obtained from the matrix ${}^{(\lambda)}\boldsymbol{Q}$ (being the usual output of semi-empirical calculations) by the transformation

$$\boldsymbol{Q}=\boldsymbol{S}^{-\frac{1}{2}}\,{}^{(\lambda)}\boldsymbol{Q}\boldsymbol{S}^{-\frac{1}{2}}\,.$$

It is also important to determine the molecular orbitals by the method which takes consequently into account the non-orthogonality of the basic atomic orbitals.

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Dr. J. Wasilewski
Professor Dr. W. Woźnicki
Institute of Physics
N. Copernicus University
Grudziądzka 5
Toruń, Poland