

# Problem of Electron Correlation in View of ESR Spectroscopy

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In the present work quantum-chemical methods for open shells in view of the description of electron correlation are studied. Spin densities are calculated on a chosen radical system and the degree of inclusion of electron correlation in individual methods with respect to the results of electron spin resonance is considered.

Systems with non-zero total magnetic moment of electrons are studied by the method of electron spin resonance. Paramagnetic nuclei contribute to the hyperfine structure of the basic spectrum corresponding to the transition between energetic levels of the appropriate magnetic moment in the outer magnetic field. The extent of their influence depends both on their magnetic moment and the distance from magnetic dipole, and it may well be calculated as the expectation value of spin Hamiltonian expressing the interaction of both the electrons and the nuclei

$$\mathfrak{H}_S = \mathfrak{H}_{is} + \mathfrak{H}_{anis}, \quad (1)$$

where the first and second term represent the Hamiltonian for isotropic or dipolar anisotropic hyperfine interaction energy.

In the radicals of organic molecules in liquids the dipolar interaction does not contribute to the hyperfine splitting and we shall only consider the expression for isotropic hyperfine interaction, the so-called Fermi's contact interaction [1]

$$\mathfrak{H}_{is} = \frac{8\pi}{3} g_e \mu_0 \mu_N \sum_{n,i} g_n \delta(\vec{r}_n - \vec{r}_i) \mathfrak{S}_n \mathfrak{S}_i, \quad (2)$$

where  $g_e$  is the  $g$  factor of the free electron (2.002319),

$g_n$  —  $g$  factor of the corresponding nucleus,

$\mu_0$  — Bohr's magneton,

$\mu_N$  — nuclear magneton,

$\delta(\vec{r}_n - \vec{r}_i)$  — Dirac's delta function,

$\mathfrak{S}_n$  a  $\mathfrak{S}_i$  — nuclear and electron spin operators.

Summation is to be made throughout all electrons and nuclei.

In a strong magnetic field in the direction of  $z$  axis, in the case of one interacting nucleus the Hamiltonian (2) may be written in the form

$$\mathfrak{H}_{is} = \frac{8\pi}{3} g_e g_N \mu_0 \mu_N \sum_i \mathfrak{S}_z(i) \mathfrak{S}_{Nz} \delta(\vec{r}_n - \vec{r}_i). \quad (3)$$

If the system is in a certain state  $\Psi$  and  $\Psi$  the eigenfunction of  $\mathfrak{S}_z = \sum_i \mathfrak{S}_i(z)$  with eigenvalue  $M_S$  we might write it

$$\mathfrak{H}_{is} = g_e \mu_0 a_N \mathfrak{S}_z \mathfrak{S}_z. \quad (4)$$

Here  $a_N$  is the constant of hyperfine splitting (further on splitting constant)

$$a_N = \frac{8\pi}{3} g_N \mu_N \rho_S(\bar{r}_N), \quad (5)$$

where  $\rho_S(\bar{r}_N)$  is the normalized spin density at the nucleus N, whereas

$$\rho_S(\bar{r}) = \langle \Psi | \sum_i \delta(\bar{r} - \bar{r}_i) \mathfrak{S}_z(i) | \Psi \rangle / M_S \quad (6)$$

is the spin density function.

Equation (6) expressed in molecular orbitals has the form [2]

$$\rho_S(\bar{r}) = \sum_i \sum_j \bar{\rho}_{ij} \psi_i^* \psi_j,$$

where  $\bar{\rho}_{ij}$  is the molecular spin density matrix. If the spin density function is written in the basis of the atomic orbitals, we should obtain

$$\rho_S(\bar{r}) = \sum_\alpha \sum_\beta \rho_{\alpha\beta} \varphi_\alpha^* \varphi_\beta,$$

where  $\rho_{\alpha\beta} = \sum_i \sum_j \bar{\rho}_{ij} c_{i\alpha} c_{j\beta}$  is the atomic spin density matrix and  $c_{i\alpha}$ ,  $c_{j\beta}$  are the coefficients in MO at the corresponding AO.

*McConnell* [2] showed that

$$a_i \sim Q \rho_i^{\text{CC}}, \quad (7)$$

where  $\rho_i^{\text{CC}}$  is the diagonal element of  $\pi$ -electron atomic spin density matrix and  $Q$  is considered to be a constant valid for all positions and radicals. Its exact theoretical value is not known. The experimental value depends on the method of spin density calculation and also on the character of the atom the appropriate hydrogen is bonded to. Thus, *Amos* and *Snyder* [3] give for  $sp^2$  the carbon atom to which other two carbon atoms are bonded,  $Q = -27$  G and for  $sp^2$ -carbon atom to which only one carbon atom (two hydrogen atoms) is bonded,  $Q = -24.4$  G.

The experimental values of splitting constants in both the anion and cation radicals of alternant hydrocarbons differ from each other. There, however, results from the symmetrical properties of molecular orbitals that in these radicals  $\rho^- = \rho^+$  the difference of the splitting constants, in view of the relation (7) cannot be explained. At present, two more complex relations for both the anion and cation radicals have been used. *Giacometti et al.* [4] admitted the contribution of the neighbouring non-diagonal members in the ion radicals not to be a negligible one. In view of the symmetry of molecular orbitals in alternant hydrocarbons, there results at once that the further member is, in its absolute value, equal for both the anion and cation radicals, the difference consisting in the sign only. We may, therefore, write

$$a_i = Q_1 c_{0i}^2 \pm Q_2 |\sum^+ c_{0i} c_{0j}|, \quad (8)$$

where + refers to positive, - to negative ions, and + at the summation sign denotes that the summation is to be performed through the neighbouring atoms with respect to  $i$ .

*Colpa* and *Bolton* [5] deduced the relation formally alike to the formula (8), the second term, however, having another significance; its origin is in quite different

physical phenomenon. These authors suggested various values of splitting constants for both the anion and cation radicals so that the electrons in C—H bond mainly "responsible" for the isotropic splitting constant do "feel" the influence of the charge on the C atom and, consequently, the sigma orbitals are different both for the positive and negative ions. This is expressed by the formula

$$a_i = Q_1 q_i + Q_2 \varepsilon_i q_i, \quad (9)$$

where  $\varepsilon_i = q_i - 1$  and  $q_i$  is the electron density on the  $i$ -th atom.

The basic idea of the "model of independent particles" is that the mutual interaction between the particles in the system may be neglected provided that the total wave function is constructed; the latter has then the simple form

$$\psi_1(x_1)\psi_2(x_2) \dots \psi_n(x_n), \quad (10)$$

where  $\psi_k$  ( $k = 1, 2, \dots, n$ ) are the spin orbitals. In fact, there is the potential  $\mathfrak{H}_{ij}$  between the  $i$  and  $j$  particles which, for small distances particularly, may acquire considerable values. If the potential has a repulsion character as the Coulomb potential  $\mathfrak{H}_{ij} = e^2/r_{ij}$  has, it is evident that it will not fail to cause the repulsion of the particles.

The situation can somehow be bettered in case the total wave function is chosen in the form of Slater's determinant; the particles with equal spins cannot be located in the same part of the space. It, therefore, remains the main problem to determine correctly the correlation between the particles with various spins.

In this respect, the electron spin resonance method proves to be of great importance since the distribution of spin density in radicals is very sensitive to correct description of electron correlation.

From this point of view, the quantum-chemical methods may be divided into two main groups. The restricted Hartree—Fock methods in which two electrons with various spins may possess a common space orbital. In this group, the most important are the *Roothaan's* [6] and *Longuet-Higgins—Pople's* methods [7]. In Roothaan's method the total wave function is the sum of antisymmetrized products, each containing one part with closed shells ( $\psi_c$ ) and one part with partially occupied shells ( $\psi_0$ ).

The Longuet-Higgins—Pople's method reminds, by the simplicity of solving open shell systems, a simple method of molecular orbitals for closed shell systems. The molecular orbitals are obtained by minimization of the energy of function

$${}^2\Psi = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2 \dots \psi_{n-1}\bar{\psi}_{n-1}\psi_n|. \quad (11)$$

When using certain approximations for matrix elements, Longuet-Higgins and Pople found that MO are the eigenfunctions of single operator analogous to closed shell operator.

This method, together with other methods solving the radicals as a closed shell problem under supplementary addition of one electron, gives positive spin densities only. For a correct description of a spin density distribution further configurations have to be added. After configuration interaction negative spin densities are obtained [8].

The method in which the problem of electron correlation for electrons with various spins is solved so that a special space orbital is attributed to each electron, is the unrestricted Hartree—Fock (UHF) method. In this method two systems of molecular

orbitals are solved, separately for electrons with  $\alpha$  and  $\beta$  spins, respectively [9–11]. Thus already the one-determinant wave function made up of these molecular orbitals

$$\Psi' = |\psi_1^\alpha \psi_2^\alpha \dots \psi_p^\alpha \psi_1^\beta \psi_2^\beta \dots \psi_q^\beta|, \quad (12)$$

where  $p$  and  $q$  is the number of electrons with  $\alpha$  and  $\beta$  spins, gives negative spin densities. This function is not, however, the eigenfunction of the square of the total spin and does not represent a pure spin state which may be obtained by the method of projection operators. *Harris* [12] starting from the projection operator

$$\mathcal{D}_S^N = \sum_{M=-S}^S \sum_{i=1}^{d_S^N} |\Theta_{SM_i}^N\rangle \langle \Theta_{SM_i}^N|,$$

where  $\Theta_{SM_i}$  is the orthonormal basis of spin functions,  $d_S^N$  is the sum of spin functions in the sub-space  $S$  and  $M$ ,  $N$  is the number of electrons in the system, determined the development coefficients for the function

$$\Psi = \mathcal{D}_S^N \Psi'$$

and deduced the relation for the calculation of spin densities following a complete projection of one-determinantal function (12)

$$e_r = \frac{1}{3 \sum_k \binom{p}{k}^{-1} \Delta_k} \sum_j^p \sum_k^q \binom{p}{k}^{-1} \Delta_k^j \left[ \frac{p+k+2}{p-k} c_{jr}^2 - c_{jr}'^2 - 2 \frac{k+1}{p-k} d_j c_{jr} c_{jr}' \right],$$

where  $d_j$  is the overlap integral between the pairs of corresponding orbitals and  $\Delta_k$  and  $\Delta_k^j$  values may be calculated from recurrent formulae

$$\Delta_k = \frac{1}{k} \sum_{p=1}^k (-1)^{p+1} \Delta_{k-p} \Theta_p$$

and

$$\Delta_k^j = \Delta_k - d_j^2 \Delta_{k-1}^j$$

at the starting values  $\Delta_0 = 1$  and  $\Delta_0^j = 1$ .  $\Theta_p$  is the auxiliary function of the form

$$\Theta_p = \sum_{i=1}^q d_i^{2p}.$$

Some simpler approaches to the symmetrization lead to further methods of spin density calculation. *Amos* and *Snyder* [13] started from the supposition that within the development

$$\psi' = \sum_{m=0}^q C'_{s'+m} \psi_{s'+m}$$

(with the lowest component  $s = s' = 1/2 (p - q)$ ), for the  $\pi$ -electron wave function of doublet states of organic molecules ( $s' = 1/2$ ), the lowest spin component has the highest weight and the coefficients belonging to the components of higher

multiplicity decrease in quite a rapid way. The component with  $s = 1/2 + 1$  affecting the spin densities to the greatest extent may simply be eliminated from the function by means of the annihilator

$$\mathfrak{D}_{s'+1} = \mathfrak{S}^2 - (s' + 1)(s' + 2).$$

The other components appear to be of little importance. The simplified expression for the spin density, which we then obtain, has the form

$$\rho_r = P_{ii} - Q_{ii} - (2/x)(\mathbf{PQP} - \mathbf{QPQ})_{ii},$$

where  $\mathbf{P}$  and  $\mathbf{Q}$  are the bond order matrices for electrons with  $\alpha$ - and  $\beta$ -spins and

$$x = (s' + 1)(s' + 2) - (1/4)(p - q)^2 + (1/2)(p + q) + \text{Tr } \mathbf{PQ}.$$

From the papers of *Malrieu* [14, 15] and *Giacometti—Orlandi* [16, 17] on the application of the second order perturbation method on the wave function (II), formulae for the calculation of spin densities were deduced, the results of which are well comparable with those obtained from the projected wave function

$$\rho_r = c_{0r}^2 + \sum_{i=1}^n [(1/3)(c_{ir}^2 - c'_{ir}{}^2) - (2/3)c_{0r}c'_{ir}S_{ni}].$$

Here,  $c_{ir}$  and  $c'_{ir}$  are the coefficients at the  $r$ -th AO in molecular orbital occupied by the electron with  $\alpha$ - and  $\beta$ -spin,  $S_{ni}$  is the overlap integral between the once occupied MO and the  $\psi_i$  orbitals.

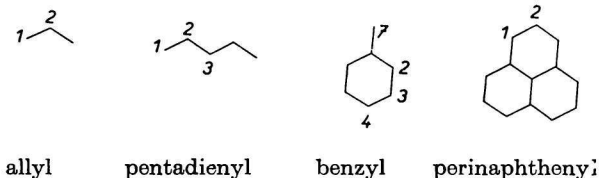
In case we use the corresponding orbitals this relation changes into [18]

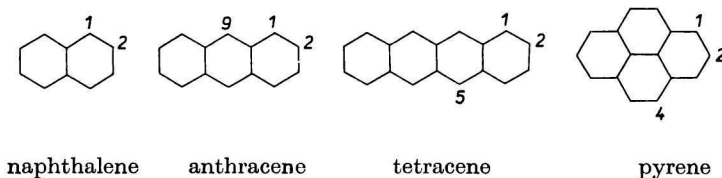
$$\rho_r = c_{0r}^2 + (1/3)\sum_i [c_{ir}^2 - c'_{ir}{}^2].$$

By these arrangements we obtain further methods for spin density calculation giving generally quite a different spin distribution. In view of this fact also the interaction parameters in the formulae (7), (8) and (9) will be the characteristics of individual methods.

#### *Calculation methods and parameters*

Spin densities were calculated by different methods (Table 1) using following parameters: Two-centre coulomb repulsion integrals were calculated according to *Nishimoto—Mataga* [19] with  $\gamma_{\text{CC}} = 11.33$  eV.  $\beta_{\text{core}}$  integrals for neighbouring positions are  $-2.39$  eV, otherwise 0





## II

The calculation was made for the radicals of the systems *I* and *II*, respectively.

### Results and Discussion

The results obtained by individual methods are shown in Table 1 from which the degree of inclusion of the electron correlation by the appropriate method may be deduced. While in the HMO method the zero spin densities are in the nonstarred positions of the alternant hydrocarbons, in the method with configuration interaction, negative spin densities will be obtained in these positions. Their values depend on the exactness degree of the appropriate method. In the unrestricted Hartree-Fock method we obtain negative spin densities even from one-determinantal wave function. As mentioned before, this function is not the eigenfunction of the total spin and the values of spin densities calculated thereby are very high. After projection of  $\Psi_{\text{UHF}}$  wave function we obtain correct values of spin densities not only in the method with a complete projection of wave function (UHF UP) but also in the other methods resulting from the simplified way of wave function symmetrization. As seen from Table 1, the values of spin densities exhibit a very small difference in these methods.

Apart from the problem of negative spin densities, the one of spin density distribution in radical plays quite an important role. It is known [20–23] that in radicals both benzyl and triphenylmethyl, in most quantum-chemical methods, for the ratio of spin densities in both *ortho* and *para* positions ( $q_o/q_p$ ), a value exceeding 1, while  $(q_o/q_p)_{\text{exp}} < 1$  is obtained. Similarly, in pentadienyl  $(q_1/q_3)_{\text{exp}} < 1$ ; the calculation results in a value exceeding 1. *Kulkarni* and *Trapp* [23] solved the problem by a simple method. They presumed that, owing to different hybridization of the carbon atom in the methyl group of these radicals, the coulomb integral ( $\alpha_{\text{Me}}$ ) has to be altered according to the formula used for heteroatoms  $\alpha_{\text{Me}} = \alpha_0 + h_{\text{Me}}\beta_0$ , where  $\alpha_0$  and  $\beta_0$  are the coulomb or resonance integrals of the carbon atom in benzene. At  $h_{\text{Me}} = -0.75$  they obtained quite a good agreement with the experiment. The calculation of spin densities in pentadienyl leads also to a good agreement with the experiment at the same  $h_{\text{Me}}$  value (Table 2). The transfer of this model into the SCF Longuet-Higgins-Pople-Lefebvre's method [7, 8] under alternation of the atomic valence state ionization potential  $W_{\text{Me}}$  with  $(\delta W_{\text{Me}} = W_{\text{Me}} - W_{\text{C}} = 2.5)$  gives correct values of spin density ratios both in benzyl and pentadienyl (Table 2).

This approach does not lead to an improvement in the UHF method. In this method, the spin density distribution in benzyl was simply improved by the fact that the wave function was projected prior to energy minimization [24]. In pentadiene there remained, however, an incorrect  $q_1/q_2$  ratio of spin densities even with such an approach.

Table 1

Spin densities in various quantum-chemical methods and corresponding experimental values of splitting constants<sup>a,b</sup>

Radical	Position	HMO	McL	LHP CI	RTH CI	UHF SD	UHF GO	UHF MSL	UHF AS	UHF UP	$a_E$
Allyl	1	0.500	0.606	0.535	0.608	0.741	0.580	0.580	0.573	0.573	-14.38
	2	0	-0.212	-0.069	-0.216	-0.483	-0.161	-0.161	-0.146	-0.146	4.06
Pentadienyl	1	0.333	0.453	0.355	0.373	0.706	0.446	0.456	0.452	0.456	-8.99
	2	0	-0.158	-0.056	-0.152	-0.502	-0.168	-0.167	-0.147	-0.153	2.65
	3	0.333	0.410	0.403	0.559	0.591	0.276	0.422	0.390	0.393	-13.40
Benzyl	2	0.143	0.164	0.177	0.107	0.465	0.276	0.232	0.245	0.244	-5.10
	3	0	-0.075	-0.023	-0.053	-0.401	-0.148	-0.134	-0.123	-0.123	1.60
	4	0.143	0.135	0.186	0.103	0.431	0.296	0.209	0.220	0.219	-6.30
	7	0.571	0.809	0.572	0.860	0.801	0.618	0.714	0.641	0.650	-16.40
Perinaphthényl	1	0.167	0.229	0.194	-	0.502	0.278	0.278	0.282	0.264	-7.30
	2	0	-0.072	-0.031	-	-0.430	-0.143	-0.143	-0.153	-0.131	2.20
Naphthalene <sup>±</sup>	1	0.181	0.229	0.204	0.223	0.298	0.224	0.231	0.231	0.230	-5.54
	2	0.069	0.043	0.057	0.035	0.005	0.046	0.037	0.037	0.037	-4.90
Anthracene <sup>±</sup>	1	0.097	0.119	0.114	0.109	0.162	0.114	0.113	0.112	0.112	-3.12
	2	0.048	0.031	0.042	0.016	-0.005	0.027	0.020	0.020	0.020	-2.76
	9	0.193	0.258	0.213	0.265	0.375	0.273	0.288	0.290	0.290	-1.40
Tetracene <sup>±</sup>	1	0.056	0.067	0.068	0.043	0.098	0.064	0.062	0.061	0.062	-6.65
	2	0.034	0.021	0.030	0.035	-0.011	0.015	0.010	0.010	0.010	-5.41
	5	0.147	0.197	0.167	0.178	0.301	0.210	0.218	0.217	0.216	-1.72
											-1.55
											-1.06
											-1.15
											-5.17
											-4.25

Table 1 (Continued)

Radical	Position	HMO	McL	LPH CI	RTH CI	UHF SD	UHF GO	UHF MSL	UHF AS	UHF UP	$a_E$
Pyrene <sup>-</sup>	1	0.137	0.189	0.154	0.162	0.379	0.220	0.231	0.229	0.230	-4.75
	2	0	-0.054	-0.024	-0.016	-0.292	-0.103	-0.097	-0.094	-0.091	1.09
	4	0.087	0.093	0.090	0.076	0.086	0.088	0.075	0.073	0.072	-3.08

a) The experimental values of splitting constants are taken from the reference [3] except the cation radical of naphthalene, which is taken from the paper [25].

b) For individual methods following markings were used:

HMO — Hückel's MO method,

RTH CI — Roothaan's method with configuration interaction,

LPH CI — Longuet-Higgins—Pople's method with configuration interaction,

McL — McLachlan's method,

UHF SD — unrestricted Hartree—Fock method with single-determinantal wave function,

UHF GO — UHF method according to Giacometti—Orlandi,

UHF MSL — UHF method according to Marshall,

UHF AS — UHF method, partial projection of the wave function according to Amos and Snyder,

UHF UP — UHF method, complete projection of the wave function according to Harris.



Table 2

Ratios of the calculated and experimental values of spin densities in pentadienyl and benzyl in McL and LHP CI methods

Method	Pentadienyl					Benzyl							
	SD			ratios		SD				ratios			
	1	2	3	$q_3/q_1$	$q_1/q_2$	2	3	4	7	$q_1/q_2$	* $q_2/q_3$		
McL	$h_{Me} = 0$	0.4526	-0.1577	0.4103	0.906	-2.870	0.1642	-0.0752	0.1352	0.8092	0.823	-2.183	
	$h_{Me} = -0.75$	0.3581	-0.1068	0.4975	1.389	-3.353	0.1889	-0.0676	0.2278	0.5258	1.206	-2.794	
LHP CI	$\delta W_c = 0$	0.3549	-0.0563	0.4028	1.135	-6.303	0.1761	-0.0277	0.1844	0.5717	1.047	-6.357	
	$\delta W_c = 2.5$	0.3321	-0.0420	0.4199	1.264	-7.907	0.1810	-0.0269	0.2013	0.5074	1.112	-6.728	
Experimental values of these ratios					1.490	-3.392						1.235	-3.188

The degree of electron correlation description may also be seen from Table 3, where separated positions with negative spin densities are shown. For the radicals of the group *I* the positions were classified according to their physicochemical properties. The first group is made up by the positions with negative spin densities,

Table 3

Interaction constants for individual position groups in *I* group radicals

Method	Positions*	$ Q $
HMO	a	—
	b	28.31
	c	40.85
LHP CI	a	57.12
	b	27.20
	c	33.44
McL	a	20.35
	b	21.29
	c	34.20
RTH CI	a	19.74
	b	21.60
	c	32.25
UHF GO	a	16.95
	b	24.19
	c	28.51
UHF MSL	a	17.37
	b	22.73
	c	28.13
UHF UP	a	19.01
	b	23.69
	c	28.66
UHF AS	a	18.47
	b	23.87
	c	28.23
UHF SD	a	5.79
	b	17.69
	c	16.14

- \* a) positions with negative spin densities,  
 b) positions in which carbon atoms bond two hydrogen atoms,  
 c) others.

the second by those in which the carbon atom is bonded to other two carbon atoms and the third by the rest of the positions. As seen from Table 3, the differences between interaction parameters of the individual groups decrease in passing from simpler methods to more exact ones.

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