THE PROBLEM OF SPIN CONTAMINATION IN UHF CALCULATIONS FOR $S = \frac{1}{2}$

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The coefficients are calculated of multiplet structure of the UHF wave function using the SCFMO method with PPP (π-approximation) and INDO approximation, resp. Parametrization influences both the values of multiplet structure coefficients and those of $\langle \mathbf{S}^2 \rangle_{\text{UHF}}$. The restrictions are discussed which set limits to the use of a quartet state annihilator as well as the influence of spin contamination upon the spin densities.

The unrestricted Hartree–Fock method[1–3] has been widely applied to the interpretation of ESR spectra in π-approximation; in the case of semiempirical all valence[4] and *ab initio* methods[5–9] the method is employed almost exclusively. In most cases one determinant wave function is considered without applying the projection or annihilation operator[10,11]. Since such function is not an eigenfunction of the $\mathbf{S}^2$ operator the question arises whether the spin densities calculated without considering the projection are of practical use. The calculated values are, in fact, exceedingly high, this being the consequence of overestimation of the spin-polarization effect in the UHF method[12,13]. Meyer[12] states that neither the spin-projected nor spin-extended wave functions are suitable for the calculation of spin densities because the projection procedure does not eliminate the excessive spinpolarization effect. The author suggested a new method which rendered better results. Brown and Williams[13] have concluded that the projection effect is restricted to the term

$$\varrho_{\text{PUHF}} \sim S(S+1)^{-1}\, \varrho_{\text{SDUHF}} = \varrho_{\text{SDUFH}}/3$$

and that any treatment leading to a reduction of spin density is equally suitable. It should be noted, however, that neither reducing nor increasing the spin densities plays a significant role in the case of semiempirical methods. Here, the agreement with experiment is achieved by using the relationship $a = Q\,.\,\varrho$, the proportionality constant being dependent on the method employed. It seems, however, that both the projection and in most cases even the annihilation, improves the results in terms of statistical evaluation[15]. In the same paper[15] and in ref.[16] it was, however, shown that the projection not always improved the results and that also the parametrization should be taken into account. The latter is capable of enhancing the spin-polarization effect[17] which usually leads to the increase in the mean value of $\mathbf{S}^2$. On the other hand, the use of *ab initio* method requires the correct values of spin densities — the statistically satisfactory values being no longer sufficient. In such a case the methods applied should be examined. Cobb and Hinchliffe[5] have shown that spin densities values obtained after the annihilation are in a poor correlation with experimental ones. The use of the formula giving approximate extended Hartree–Fock results yields values that are in a good agreement with the experiment[5]. Since the orbitals of the projected wave function are not reoptimised the depreciation of the results may occur even at a slight spin-contamination. Similar danger exists when using the annihilation operator. Moreover, here the correctness of results will depend on the validity of assumption that $C_S \sim 0$ or $S < 3/2$ in the component expansion of the UHF wave function

$$\psi_U = \sum_{S=M}^{N/2} C_S \psi_S , \tag{1}$$

where N denotes the number of electrons; $M = 1/2(p - q)$; p and q being the number of electrons with α and β spins, resp. It seems that this condition is not always fulfilled[17,18].

It was a purpose of this work to make a component analysis of expansion (*1*), to examine the dependence of expansion coefficients upon parameters and to show the applicability of projection or annihilation procedure for the spin density calculations.

PROBLEM FORMULATION

The projection operator $\mathbf{O}_S$ will separate[10] the component describing the pure spin state from the wave function (*1*)

$$\psi = \mathbf{O}_S \psi_U = C_S \psi_S \tag{2}$$

where

$$\psi_U = |\chi_1(1)\,\alpha(1) \ldots \chi_p(p)\,\alpha(p)\,\eta_1(p+1)\,\beta(p+1 \ldots .\,\eta_q(p+q)\,\beta(p+q)|$$

χ_i a η_i being corresponding orbitals[19] defined as

$$\begin{gathered} \langle \chi_i, \chi_j \rangle = \langle \eta_i, \eta_j \rangle = \delta_{ij} \\ \langle \chi_i, \eta_j \rangle = \lambda_i \delta_{ij} \,. \end{gathered} \tag{3}$$

Then

$$\langle \psi, \psi \rangle = C_S^2 = \omega_S \,, \quad \langle \psi_U, \psi_U \rangle = \sum_S \omega_S = 1$$

and

$$\langle \mathbf{S}^2 \rangle_U = \sum_S \omega_S S(S+1) \,, \quad E = \sum_S \omega_S E_S \,.$$

The expression for ω_S was derived by Sasaki–Ohno[20]

$$\omega_S = \sum_{k=0}^{n-M} (-1)^k \, C_k(S, M, n) \, A_k \,, \tag{4}$$

where $2n = p + q = N$,

$$C_k(S, M, n) =$$

$$= \frac{4S+2}{2S+n+2} \sum_{j=0}^{S-M} (-1)^{S+M+k-j} \binom{S-M}{j} \binom{S+M}{S-M-j} \binom{n+S}{p+j-k}^{-1} . \tag{5}$$

A_k being the sum of products of overlap integral squares between pairs of correspoding orbitals[21,22].

$$A_k = \sum_{\{i\}_k} \prod_i |\langle \chi_i, \eta_i \rangle|^2 = \sum_{\{i\}_k} \prod_i \lambda_i^2 \, , \tag{6}$$

k expressing the number of exchanges between electrons possessing α and β spins, resp.

The aplication of the annihilation operator of the quartet component $A_{3/2}$ to the UHF wave function[11] results in expression

$$A_{3/2}\psi_U = \sum_S C_S[S(S+1) - (M+1)(M+2)]\,\psi_S = \sum_S C_S B_S \psi_S \tag{7}$$

and

$$\langle \mathbf{S}^2 \rangle_{aa} = \sum_S \omega_S^2 B_S^2 S(S+1) \, .$$

The requirement of the mean value of $\mathbf{S}^2$ being lower after annihilation leads to the inequality

$$\omega_{1/2}\omega_{3/2} > \frac{1}{27} \sum_{\substack{S<S' \\ S=M \\ S'=5/2}} \omega_S \omega_{S'} \, (B_S^2 - B_{S'}^2) \, (S(S+1) - S'(S'+1)), \tag{8}$$

B_S being defined by equation (7).

TABLE I

Coefficients ω_S and the Values of $\langle \mathbf{S}^2 \rangle$ of Some Radicals Obtained by the PPP Treatment

Radical	Method	β, eV	ω_S				$\langle \mathbf{S}^2 \rangle_U$	$\langle \mathbf{S}^2 \rangle_{aa}$
			$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$		
	PP	−2·39	0·97282	0·02718			0·83154	0·75
Allyl		−2·39	0·92226	0·07773			0·98320	0·75
	NM	−1	0·74026	0·25973			1·52920	0·75
	PP	−2·39	0·93990	0·05951	0·00058		0·93322	0·76381
Pentadienyl		−2·39	0·83224	0·16209	0·00566		1·28158	0·89840
	NM	−1	0·57746	0·36155	0·06099		2·32255	2·56463
	PP	−2·39	0·97113	0·02865	0·00022	0·00000	0·83770	0·75503
Benzyl		−2·39	0·84017	0·15209	0·00764	0·00010	1·26888	0·97403
	NM	−1	0·48282	0·38798	0·11709	0·01211	3·03228	6·24823
	PP	−2·39	0·89643	0·10125	0·00230	0·00001	1·07235	0·81009
Heptatrienyl		−2·39	0·74415	0·23657	0·01887	0·00041	1·61680	1·39455
	NM	−1	0·47175	0·39108	0·12353	0·01364	3·11607	6·57554

Since there is always a product of two coefficients (ω_S, $\omega_{S'}$) on the right-hand side, one of them being close to zero, the inequality (*8*) is well obeyed in such cases where Amos–Snyder[11] assumptions are valid. As soon as ω_S for $\boldsymbol{S} \geqq 5/2$ is no longer negligible, the inequality is not necessarily fulfilled and the value of $\langle \boldsymbol{S}^2 \rangle$ will increase after annihilation.

RESULTS AND DISCUSSION

Coefficients ω_S will be calculated from relation (*4*). Claxton[23] and coworkers suggested another method of calculation of the coefficient ω_S; the method is based on the use of annihilators of various multiplets and on the calculation of corresponding $\langle \boldsymbol{S}^2 \rangle_{aa}$ values. Corresponding values of A_k are calculated by means of a recurrent relationship[14,21,22]

$$A_k = \frac{1}{k} \sum_r^k (-1)^{r+1} A_{k-r} \theta_r \, . \qquad (9)$$

Where $A_0 = 1$ and θ_r is an auxiliary function[21,22]

$$\theta_r = \sum_{k=1}^{q} \lambda_k^{2r} \, ,$$

TABLE II

The Analysis of Linear Dependence Between Experimental Values of Hyperfine Splitting Constants and Spin Densities Calculated by PPP and INDO Methods

PPP method

Method	β, eV	No of points	UHF SD		PUHF		UHFAA	
			Corr. coef.	Standard deviation	Corr. coef.	Standard deviation	Corr. coef.	Standard deviation
PP	−2·39	11	0·982	1·115	0·975	1·312	0·975	1·305
NM	−1	11	0·890	4·773	0·916	3·354	0·844	4·513
	−2·39	11	0·939	2·030	0·977	1·255	0·970	1·429

INDO method

Method	No of points	Corr. coef.		Standard deviation	
		Pople	Kaufman	Pople	Kaufman
UHF SD	28	0·993	0·966	3·56	9·11
PUHF	28	0·986	0·995	6·43	3·57

The coefficients ω_S calculated for several radicals in the π-approximation by the PPP method are presented in Table I. It follows that a change in γ-integrals causes a significant changes both in $\langle S^2 \rangle_U$ and ω_S coefficients. When using the Nishimota–Mataga[24] approximation (NM) the value of $\langle S^2 \rangle_U$ is declining more from 0·75 than in the case of Pariser–Parr approximation[25]. In the latter approximation the assumptions of Amos–Snyder about the negligible contribution of higher multiplicity components are better fulfilled.

Thus it can be expected that the projection* will substantially affect the results of spin densities when using the Nishimota–Mataga approximation where the spin contamination is higher. This conclusion is confirmed by the values tabulated in Table II.

Similar results are obtained when the INDO method is applied for various values of Slater-Condon parameters[15] (SCP). In the original parametrization procedure due to Pople, the spin densities are changed only slightly after projection. When, however, the Kaufman procedure is applied for SCP, the projection leads to marked improvement of results (Table II).

Similarly to the PPP method, the value of $\langle S^2 \rangle_U$ is lower in the case of Pople parametrization which gives better results without the projection of wave function (Table III). Also the corresponding expansion coefficients $\omega_{1/2}$ in equation (*1*) are higher.

In cases where $\langle S^2 \rangle_U$ approaches the value of 0·75 the projection does not lead to the improvement of results. This may be due to the fact that the projected wave function, although being the eingenfunction of the S^2 operator, consits of non-reoptimized molecular orbitals.This may have a considerable influence at a slight spin

TABLE III

Coefficients ω_S and Values $\langle S^2 \rangle$ in the INDO Method

Radical	Kaufman			Pople		
	$\langle S^2 \rangle_U$	$\langle S^2 \rangle_{aa}$	$\omega_{1/2}$	$\langle S^2 \rangle_U$	$\langle S^2 \rangle_{aa}$	$\omega_{1/2}$
Vinyl	0·785	0·751	0·989	0·763	0·750	0·996
Isobutyronitril	0·802	0·752	0·983	0·784	0·750	0·989
Benzyl	0·859	0·759	0·964	0·809	0·753	0·977
Allyl	0·851	0·753	0·967	0·824	0·751	0·975

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* A complete projection of the wave function was carried out using the method due to Harris[21,22].

contamination. The spin densities calculated from the projected wave function are substantially different from those obtained from the extended wave function[26].

The spin contamination is a function of the method applied and of parameters considered. Table I shows the values of $\langle \mathbf{S}^2 \rangle$ and ω_S for the case* of $\beta = -1$ eV. The values of $\langle \mathbf{S} \rangle_U$ are high and they are increased even more by the annihilation. This holds for the cases where $\omega_{1/2}$ is low and ω_S are nonzero for $\mathbf{S} > \frac{3}{2}$. In these cases the inequality (8) is not fulfilled. It can be expected that in such case the spin densities will be worse after the annihilation, rather than before it. On the other hand, the projection improves the values of spin densities in cases of substantial spin contamination. This is because of the removing of indesirable components which predominates over the devaluation of wave function with regard to the energetic minimum. The values of correlation coefficients in Table II together with those of $\langle \mathbf{S}^2 \rangle$ in Table I only confirm these conclusions. In all considered cases of radicals (except allyl) the spin contamination at $\beta = -1$ eV increases after the annihilation (Table I). This leads eventually to the inferior results.

TABLE IV

The Values of λ, $\langle \mathbf{S}^2 \rangle$, and $\omega_{1/2}$ for a Benzyl Radical Calculated by the PPP Method

Method	β, eV	λ_1[a]	λ_2	λ_3	$\langle \mathbf{S}^2 \rangle_U$	$\omega_{1/2}$
NM	−2·39	0·96513	0·89542	0·86479	1·268877	0·8402
	−1	−0·63290	−0·43505	0·35761	3·032286	0·4828
PP	−2·39	−0·99608	−0·98290	−0·97674	0·837703	0·9711
	−1	0·83352	0·65176	−0·56907	2·306614	0·5977

[a] $\lambda_i = \langle \chi_i | \eta_i \rangle$.

TABLE V

The Dependence of $\langle \mathbf{S}^2 \rangle_U$ Calculated by the INDO Method upon the R_{C-H} in the Methyl Radical

R_{C-H}, Å	0·8	0·9	1·0	1·1	1·2	1·3.	1·4	1·5	1·6	1·7
$\langle \mathbf{S}^2 \rangle_U$	0·753	0·753	0·754	0·756	0·759	0·764	0·774	0·800	0·866	1·044

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* This idea was first presented by Burnham[17] who found a strong dependence of $\langle \mathbf{S}^2 \rangle$ upon β.

The influence of parameters on the value of $\langle \boldsymbol{S}^2 \rangle_U$ indicates a direct connection between parameters and values of λ_i which reflect the extent of the molecular orbital decoupling. When $\lambda_i \sim 1$ then $\omega_{1/2} \sim 1$ and other components (except quartet) do not practically contribute to ψ_U in (*1*). This is true for cases in which inequality (*8*) holds *e.g.* π-approximation in PPP method (PP) (Table I), the INDO method when considering semiempirical SCP (Table III). In these cases the spin densities upon the annihilation are identical with those obtained after the projection. When increasing the values of exchange integrals in INDO method[15] (Table III) and extending the interatomic distances directly[27] or indirectly (*via* integrals β and γ) (Table I, II*b*) the values of λ_i are decreasing together with $\omega_{1/2}$ while $\langle \boldsymbol{S}^2 \rangle$ increases (Table IV).

Sasaki and Ohno[20] studied the dependence of ω_S on the number of electrons. Unfortunately, the real curve describing this dependence can be plotted without difficulties for a given number of electrons only in the orthogonal system. The values of $\langle \boldsymbol{S}^2 \rangle_U$ were calculated for a series of radicals derived from aliphatic hydrocarbons going from methyl to nonyl. We have found that for this number of electrons the $\langle \boldsymbol{S}^2 \rangle_U$ values are independent of the number of electrons, the average value of $\langle \boldsymbol{S}^2 \rangle_U$ being found 0·755–0·758. On the other hand, there is undoubtedly a dependence between the value of $\langle \boldsymbol{S}^2 \rangle_U$ and the interatomic distance, similarly as found in ref.[27] (Table V).

CONCLUSION

The value of $\langle \boldsymbol{S}^2 \rangle$ in the UHF method is a function of many factors whose common feature is the decoupling of molecular orbitals. It can be expected that any operation which enhances the decoupling of MO (decreasing values of λ) such as high exchange integrals, long interatomic distance, low absolute values of β-integrals, low value of γ-integrals, will, in the case of the UHF method, lead to the increased spin contamination.

The method of annihilation of quartet state at low spin contamination yields results that are identical with those obtained after a complete projection. At high spin contamination the annihilation gives worse results than the complete projection and in cases where inequality (*8*) is not fulfilled the results are worse than those obtained by the UHF.

The method of a complete projection improves spin densities when the values of $\langle \boldsymbol{S}^2 \rangle_U$ are high. In the opposite case the effect of deviation from the energetic minimum comes into play and the results of UHF SD treatment are better. Therefore, in cases where there is a considerable spin contamination it is advantageous to use a complete projection of the wave function while in other cases the UHF treatment will suffice without the projection. When more accurate results are required, it becomes necessary to apply the more precise extended Hartree–Fock method.

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