Theoret. chim. Acta (Berl.) 13, 428–432 (1969)

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Spin Contamination in PPP Unrestricted Hartree-Fock Wave Functions

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Received January 27, 1969

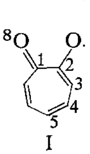
A case is reported in which a normal parametrisation of a PPP UHF calculation for a free radical leads to a value of $\langle S^2 \rangle$ which increases on the annihilation of the contaminating quartet component.

The Unrestricted Hartree-Fock (UHF) method for $p\alpha$ and $q\beta$ spin electrons yields a wave function Ψ_{UHF} which is not an eigenfunction of S^2 since it contains components of multiplicity greater than $(p-q)+1$. The wave function may be expanded as a sum of determinants

$$\Psi_{\mathrm{UHF}} = \sum_{m=0}^{q} C_{s+m} \psi_{s+m}$$

where $s = \frac{1}{2}(p-q)$ and ψ_{s+m} represents the component of multiplicity $2(s+m)+1$. The coefficients, C_{s+m}, decrease rapidly as m increases and in many cases the only significant contaminant is ψ_{s+1} and annihilation of this component [1, 2], rather than the projection of ψ_s [3], is sufficient for most purposes. A good correlation has been found between the spin densities after annihilation and the observed ESR hyperfine splitting constants for a wide range of organic radicals [2, 4].

In π-electron calculations the expectation values of S^2 indicate that spin contamination is generally small and $\langle S^2 \rangle$ is improved by annihilation. It can be seen, however, that $\langle S^2 \rangle$ is in general not as good for neutral radicals as it is for charged species [2, 5]. We wish to report a PPP [6] calculation on the tropoloxyl radical (I) in which $\langle S^2 \rangle$ is closer to $\frac{3}{4}$



I

before annihilation of the major contaminant, the quartet, than after this operation. This occurs when the two centre repulsion integrals, γ_{pq}, are calculated by the method of Mataga and Nishimoto (MN) [7]

$$\gamma_{pq} = 14.395/(a_{pq} + r_{pq})$$

but not if these integrals are approximated by the charged spheres (CS) method [6, 8] (Table 1). In an attempt to gain a better understanding of this, the pentadienyl radical has been investigated. With $\beta_{CC} = -2.39$ eV and MN integrals, normal values of $\langle S^2 \rangle$ are obtained but if β_{CC} is reduced to -1.0 eV $\langle S^2 \rangle$ is greater after annihilation than before. In this case an improvement in $\langle S^2 \rangle$ can be obtained by annihilation of the sextet. The annihilator for the component of multiplicity $2(s+j)+1$ is

Table 1. $\langle S^2 \rangle$ *Before and after annihilation*[a]

	Tropoloxyl[b]		Pentadienyl			
β_{CC} in eV	-2.301		-2.39		-1.0	
Calcul No.	A	B	A	B	C	D
γ_{pq}	CS	MN	CS	MN	CS	MN
$\langle S^2 \rangle_{SD}$	1.12873	1.78083	0.91040	1.26218	1.88571	2.32255
$\langle S^2 \rangle_{AAQ}$	0.86123	1.91505	0.76179	0.88940	1.64176	2.56492
$\langle S^2 \rangle_{AAS}$	0.89667	1.14430	0.81312	0.95388	1.19370	1.33945
$\langle S^2 \rangle_{MIN}$	0.81554	1.08823	0.75996	0.83455	1.06361	1.23146
a_{MIN}	4.832	6.699	4.072	4.742	5.938	6.616
$\langle H \rangle_{SD}$ eV	-223.520	-168.054	-70.001	-50.638	-63.399	-45.246
$\langle H \rangle_{SD}$ eV[c]	-220.923	-166.103	-66.511	-47.818	-62.466	-44.596

[a] Abbreviations: SD = single determinant, AAQ = after annihilation of quartet, AAS = after annihilation of sextet, MIN = Minimum value of $\langle S^2 \rangle$ using the annihilator $S^2 - a$.

[b] $\beta_{C-O} = -2.262$ eV, $U_O - U_C = -6.54$ eV.

[c] Quartet state.

$$A_{s+j} = S^2 - (s+j)(s+j+1)$$

and the wave function after annihilation is

$$A_{s+j} \Psi_{UHF} = \sum_{m=0}^{q} (m-j)(m+j+2s+1)\, C_{s+m} \psi_{s+m} .$$

After annihilation of the quartet, the wave function has a greater proportion of the components with high multiplicity (Table 2). Consequently, unless the C_{s+m} decrease sufficiently rapidly, the increase in the contribution to $\langle S^2 \rangle$ from the terms of high multiplicity more than compensates for the removal of the quartet.

The common feature in the two cases where $\langle S^2 \rangle$ increases on annihilation of the quartet is that the effect is produced by a reduction in the magnitude of the off-diagonal elements of the F matrices, the most marked change being in those elements corresponding to bonded atoms. This results in a lowering of the energy of the excited quartet, sextet etc. (Table 1) and an increase in the population of these states. This is reflected in the increased population numbers of the high energy general spin orbitals when $\langle S^2 \rangle$ is large (Table 3).

The large contamination of the wave function has a marked effect on the magnitudes of the spin densities but not on the general form of the spin distribution which also appears to be largely independent of the component annihilated. Since the unrestricted wave function may be expanded in terms of a restricted function,

Table 2. *Squares of the normalized coefficients of the spin components*

Component, $S =$		$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
Pentadienyl						
Calcul A	SD	0.947	0.052	0.001	—	—
	AAQ	0.999	0.000	0.001	—	—
	AAS	0.979	0.021	0.000	—	—
Calcul B	SD	0.837	0.159	0.004	—	—
	AAQ	0.986	0.000	0.014	—	—
	AAS	0.931	0.069	0.000	—	—
Calcul C	SD	0.655	0.325	0.020	—	—
	AAQ	0.921	0.000	0.079	—	—
	AAS	0.838	0.162	0.000	—	—
Calcul D	SD	0.578	0.362	0.061	—	—
	AAQ	0.773	0.000	0.227	—	—
	AAS	0.804	0.197	0.000	—	—
Tropoloxyl						
Calcul A	SD	0.881	0.115	0.004	0.000	0.000
	AAQ	0.987	0.000	0.012	0.001	0.000
	AAS	0.951	0.049	0.000	0.000	0.000
Calcul B	SD	0.709	0.261	0.029	0.001	0.000
	AAQ	0.876	0.000	0.098	0.025	0.000
	AAS	0.873	0.125	0.000	0.001	0.000

Table 3. *Natural orbitals and their occupation numbers*

Pentadienyl	Coefficients			Occupation numbers			
Radical	1,5	2,4	3	SD	AAQ	AAS	AAD
Calcul A	0.3032	0.5	0.5623	1.9784	1.9908	—	—
	±0.5	±0.5	0.0	1.9394	1.9760	—	—
	0.5623	0.0	−0.6064	1.0000	1.0000	—	—
Calcul D	0.2855	0.5	0.5805	1.5515	1.5226	1.6307	1.2027
	±0.5	±0.5	0.0	1.3511	1.3610	1.4194	1.1024
	0.5805	0.0	−0.5710	1.0000	1.0000	1.0000	1.0000

Tropoloxyl Radical	Coefficients					Occupation numbers	
	1,2	3,7	4,6	5	8,9	SD	AAQ
Calcul A	0.3092	0.3380	0.4016	0.4203	0.2012	1.9858	1.9913
	±0.3220	∓0.3380	∓0.2292	0.0	±0.4783	1.9841	1.9903
	0.3917	0.0435	−0.2979	−0.4523	0.3920	1.9488	1.9710
	±0.0770	±0.3668	±0.4324	0.0	±0.4154	1.8836	1.9406
	0.1352	0.4357	−0.2333	−0.4268	−0.4475	1.0000	1.0000
Calcul B	0.3236	0.3526	0.3961	0.4109	0.1721	1.9433	1.9336
	±0.3447	∓0.3843	∓0.2338	0.0	±0.4229	1.9359	1.9260
	0.4069	0.0816	−0.3023	−0.4862	0.3438	1.8505	1.8500
	±0.1116	±0.3279	±0.4280	0.0	±0.4437	1.6928	1.7401
	0.1102	0.3918	−0.0182	−0.3832	−0.5105	1.0000	1.0000

(r.f.), and single (s.e.) and double excitations (d.e.) [2]:

$$\Psi_{\mathrm{UHF}} = C^{\mathrm{r.f.}}_{\frac{1}{2}} \psi^{\mathrm{r.f.}}_{\frac{1}{2}} + C^{\mathrm{s.e.}}_{\frac{1}{2}} \psi^{\mathrm{s.e.}}_{\frac{1}{2}} + C^{\mathrm{s.e.}}_{\frac{3}{2}} \psi^{\mathrm{s.e.}}_{\frac{3}{2}} + C^{\mathrm{d.e.}}_{\frac{1}{2}} \psi^{\mathrm{d.e.}}_{\frac{1}{2}} + C^{\mathrm{d.e.}}_{\frac{3}{2}} \psi^{\mathrm{d.e.}}_{\frac{3}{2}} + C^{\mathrm{d.e.}}_{\frac{5}{2}} \psi^{\mathrm{d.e.}}_{\frac{5}{2}} + \cdots$$

the major matrix elements of the spin density operator, ϱ, between components of different multiplicity must give rise to a spin distribution of the same form as the doublet. On annihilation of the quartet, the most important of these terms is $\langle \psi^{\mathrm{s.e.}}_{\frac{1}{2}} | \varrho | \psi^{\mathrm{d.e.}}_{\frac{5}{2}} \rangle$ while annihilation of the sextet gives three non-zero elements,

$$\langle \psi^{\mathrm{r.f.}}_{\frac{1}{2}} | \varrho | \psi^{\mathrm{s.e.}}_{\frac{3}{2}} \rangle, \quad \langle \psi^{\mathrm{s.e.}}_{\frac{1}{2}} | \varrho | \psi^{\mathrm{s.e.}}_{\frac{3}{2}} \rangle \quad \text{and} \quad \langle \psi^{\mathrm{s.e.}}_{\frac{3}{2}} | \varrho | \psi^{\mathrm{s.e.}}_{\frac{3}{2}} \rangle ,$$

with coefficients of magnitude at least comparable to that of $\langle \psi^{\mathrm{s.e.}}_{\frac{1}{2}} | \varrho | \psi^{\mathrm{d.e.}}_{\frac{5}{2}} \rangle$. This is consistent with the observation that, even for the pentadienyl calculation *D*, the best spin densities are obtained by annihilation of the quartet and not the sextet.

Table 4. *Spin densities*

	Allyl, $\beta = -2.39$ eV CS		Pentadienyl, Calcul D		
	1	2	1	2	3
Single det	0.6476	−0.2952	0.9411	−0.8853	0.8882
AAQ	0.5457	−0.0912	0.4648	−0.1752	0.4208
AAS	—	—	0.8500	−0.7414	0.7827
AAD	0.3333	0.3333	0.5768	−0.3731	0.5926
Minimum value of S^2	—	—	0.7781	−0.6331	0.7099
Expt[a]	0.582	0.164	0.345	−0.102	0.514

[a] From splitting constants given in Ref. [9] for the allyl and cyclohexadienyl radicals with Q obtained by fitting to the overall spectrum width.

The suggestion [1] that a mixture of components should be projected from the UHF wavefunction using the annihilator $S^2 - a$, where a is chosen to minimise $\langle S^2 \rangle$, leads to no improvement in the computed spin densities. The minimum values of $\langle S^2 \rangle$ are given in Table 1 together with the corresponding values of a. In those cases where $\langle S^2 \rangle_{\mathrm{AAQ}}$ is close to 0.75 the minimum value of $\langle S^2 \rangle$ corresponds, almost entirely, to annihilation of the quartet and consequently there are only small changes in the spin densities. However in those cases where $\langle S^2 \rangle_{\mathrm{AAQ}}$ is large, the required annihilation falls between the quartet and sextet components and there are large differences between these spin densities and those obtained by annihilation of the quartet only. However it is suggested above that the spin density on annihilation of the quartet leads to the best agreement with experiment and there seems to be no reason to modify this view (Table 4). Finally it should be noted that the first evidence that the UHF wavefunction in the PPP approximation may be critically dependent on the integral approximations used, comes from the singlet ground state work of Koutecký [10].

The author would like to thank Dr. B. T. Sutcliffe for many helpful discussions and Dr. A. Hinchliffe for his spin annihilation routine. I.C.I. Ltd. are thanked for a Research Fellowship and the referee for his comments.

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Theoret. chim. Acta (Berl.) 13,432 (1969)

Erratum

Calculation of Hyperfine Field and Quadrupole Splitting in Ferriprotoporphyrin IX Chloride (Hemin)

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Theoret. chim. Acta (Berl.) **12**, 178—182 (1968)

Received March 17, 1969

The sign of q in Eq. (7) is incorrect, necessitating the following changes: 1. the summation in Eq. (7) should be preceded by a minus sign; 2. the first two lines after Eq. (8) should have $q = -.6626 a_0^{-3}$ and $\Delta E = -.73$ mm/sec; 3. in the table on p. 181, the column headings should be preceded by minus signs; 4. in the first line after this table, replace the word "positive" by "negative", and in the third line replace "negative" by "positive".

In view of these corrections, our remarks concerning good agreement of experimental and theoretical field gradient no longer apply. The conclusions concerning hyperfine field at iron are unchanged, however. Further discussion of the experimental and theoretical field gradients will be given in a forthcoming paper on N^{14} hyperfine and quadrupole interactions in hemin, to be submitted to this journal.

We are grateful to Dr. T. Moss of the IBM-Watson Laboratory, New York, for bringing the error to our attention.