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The Restriction of Spin Contamination in Unrestricted Hartree Fock Wave Functions

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A method is developed to study in detail the contaminating spin components in UHF calculations for free radicals. Applications are made to those cases previously reported in which normal parametrisation of PPP UHF calculations lead to values of $\langle S^2 \rangle$ which increase on annihilation of the contaminating quartet component.

Es wird eine Methode entwickelt, um detaillierte Untersuchungen der bindenden Spinkomponenten in UHF-Rechnungen für freie Radikale zu ermöglichen. Es werden Anwendungen für solche Fälle, über die schon früher einmal berichtet wurde, durchgeführt, bei denen die normale Parametrisierung von PPP-UHF-Rechnungen zu Werten von $\langle S^2 \rangle$ führte, welche die Vernichtung der bindenden Quartettkomponente anwachsen lassen.

Développement d'une méthode pour étudier en détail les composantes de spin étrangères dans les calculs UHF des radicaux libres. On l'applique aux cas précédemment considérés dans lesquels des calculs UHF avec paramétrisation PPP conduisent à des valeurs de $\langle S^2 \rangle$ qui croissent lorsque l'on annule la composante quartet.

It is well known that the unrestricted Hartree Fock (UHF) wave function is not an eigenfunction of the $\boldsymbol{S}^2$ operator, and may be expanded as a sum of pure spin states [1],

$$\Psi_{\mathrm{UHF}} = \sum_{m=0}^{j} c_{s+m} \Phi_{s+m} \tag{1}$$

where i and j are the number of α and β spin electrons respectively, $i \geqq j$ and $s = \frac{1}{2}(i-j)$.

It has been shown that the major contaminating component is usually that of spin $s+1$, and that the c_{s+m} coefficients decrease rapidly with m. This led Amos and Hall [1] to suggest that the application of the annihilator A_{s+1} to Ψ_{UHF} would result in improved spin density distributions and $\langle \boldsymbol{S}^2 \rangle$ values. Although this method has enjoyed considerable success [2, 3], the work of Sasaki and Ohno [4] indicated that the procedure may fail in certain cases, and recently Burnham [5] has reported calculations in which the value of $\langle \boldsymbol{S}^2 \rangle$ obtained from Ψ_{UHF} is unreasonably large and which increases on applying the annihilator A_{s+1}.

Because of the difficulty of annihilating unwanted spin components before minimisation, Burnham [5] has followed the normal procedure of minimising the function

$$E_{\mathrm{UHF}} = \frac{\langle \Psi_{\mathrm{UHF}} | \boldsymbol{H} | \Psi_{\mathrm{UHF}} \rangle}{\langle \Psi_{\mathrm{UHF}} | \Psi_{\mathrm{UHF}} \rangle} \tag{2}$$

and subsequently applies the annihilator, A_{s+1}, to the wavefunction obtained. This procedure does not impose any restriction on $\langle S^2\rangle_{\mathrm{UHF}} = \langle \Psi_{\mathrm{UHF}}|S^2|\,\Psi_{\mathrm{UHF}}\rangle$. To overcome this Claxton and McWilliams [6] have suggested that it is practical to minimise a function of the type

$$\alpha E + (1-\alpha)\langle S^2\rangle \tag{3}$$

where E can be either E_{UHF} or

$$E_{s+1} = \frac{\langle \Psi_{\mathrm{UHF}}|H|A_{s+1}\,\psi_{\mathrm{UHF}}\rangle}{\langle \Psi_{\mathrm{UHF}}|A_{s+1}\,\Psi_{\mathrm{UHF}}\rangle} \tag{4}$$

and $\langle S^2\rangle$ can be either $\langle S^2\rangle_{\mathrm{UHF}}$ or

$$\langle S^2\rangle_{s+1} = \frac{\langle \Psi_{\mathrm{UHF}}|S^2|A^2_{s+1}\,\Psi_{\mathrm{UHF}}\rangle}{\langle \Psi_{\mathrm{UHF}}|A^2_{s+1}\,\Psi_{\mathrm{UHF}}\rangle} \tag{5}$$

and $0<\alpha<1$.

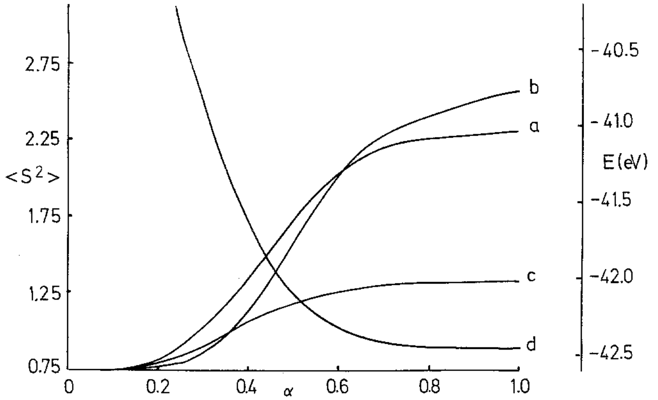

Fig. 1. Pentadienyl ($\beta_{\mathrm{CC}} = -1$ eV). Results from ψ_{UHF} obtained by the minimisation of $\alpha E_{\mathrm{UHF}} + (1-\alpha)\langle S^2\rangle_{\mathrm{UHF}}$. a) $\langle S^2\rangle_{\mathrm{UHF}}$, b) $\langle S^2\rangle_{1.5}$, c) $\langle S^2\rangle_{2.5}$, d) E_{UHF}

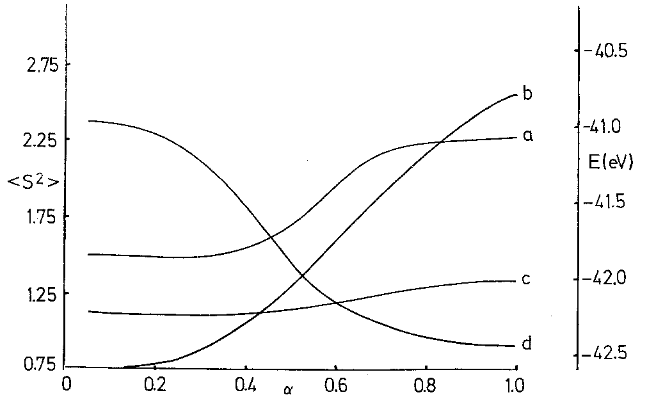

Fig. 2. Pentadienyl ($\beta_{\mathrm{CC}} = -1$ eV). Results from ψ_{UHF} obtained by the minimisation of $\alpha E_{\mathrm{UHF}} + (1-\alpha)\langle S^2\rangle_{1.5}$. a) $\langle S^2\rangle_{\mathrm{UHF}}$, b) $\langle S^2\rangle_{1.5}$, c) $\langle S^2\rangle_{2.5}$, d) E_{UHF}

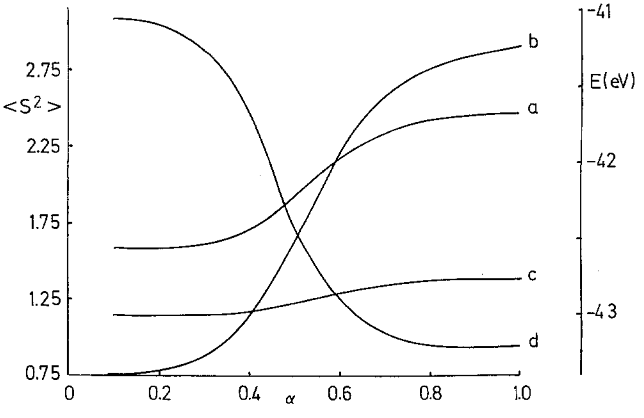

Fig. 3. Pentadienyl ($\beta_{CC} = -1$ eV). Results from ψ_{UHF} obtained by the minimisation of $\alpha E_{1.5} + (1-\alpha)\langle S^2\rangle_{1.5}$. a) $\langle S^2\rangle_{UHF}$, b) $\langle S^2\rangle_{1.5}$, c) $\langle S^2\rangle_{2.5}$, d) $E_{1.5}$

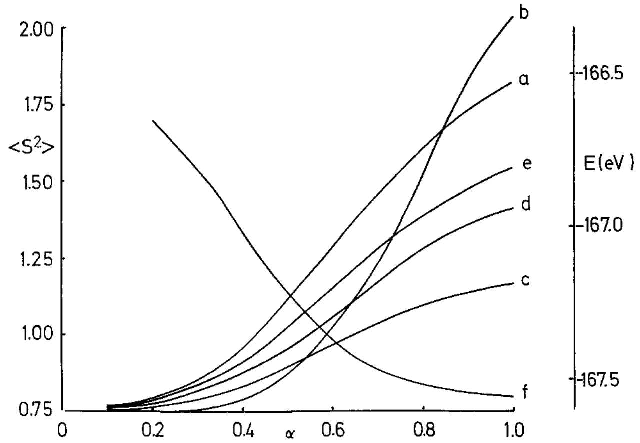

Fig. 4. Tropoloxyl. Results from ψ_{UHF} obtained by the minimisation of $\alpha E_{UHF} + (1-\alpha)\langle S^2\rangle_{UHF}$. a) $\langle S^2\rangle_{UHF}$, b) $\langle S^2\rangle_{1.5}$, c) $\langle S^2\rangle_{2.5}$, d) $\langle S^2\rangle_{3.5}$, e) $\langle S^2\rangle_{4.5}$, f) E_{UHF}

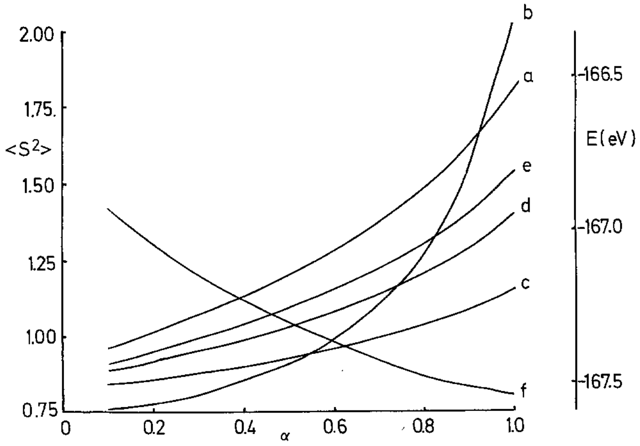

Fig. 5. Tropoloxyl. Results from ψ_{UHF} obtained by the minimisation of $\alpha E_{UHF} + (1-\alpha)\langle S^2\rangle_{1.5}$. a) $\langle S^2\rangle_{UHF}$, b) $\langle S^2\rangle_{1.5}$, c) $\langle S^2\rangle_{2.5}$, d) $\langle S^2\rangle_{3.5}$, e) $\langle S^2\rangle_{4.5}$, f) E_{UHF}

A given value of α then results in a particular value of $\langle S^2 \rangle$ and the energy, E, is the minimum obtainable for that value of $\langle S^2 \rangle$. The results of Burnham [5] are equivalent to using $\alpha = 1$ and $E = E_{\mathrm{UHF}}$. The use of a small value of α results in a reduced value for $\langle S^2 \rangle$, an improvement which is obtained at the expense of a higher energy (see Figs. 1–5).

We have repeated the calculations on the tropoloxyl and pentadienyl radicals, which were carried out by Burnham [5]. All bond lengths were taken as 1.4 Å and idealised geometries were used. The integrals of Nishimoto and Mataga [7] were used throughout ($\gamma_{\mathrm{CC}} = 11.13$ eV and $\gamma_{\mathrm{OO}} = 15.23$ eV). For the tropoloxyl radical β_{CC} was taken as -2.301 eV, β_{CO} as -2.262 eV and $u_{\mathrm{O}} - u_{\mathrm{C}}$ as -6.54 eV; for the pentadienyl radical β_{CC} was taken as -1.0 eV after Burnham [5].

The minimisations were carried out by the method of steepest descents to a convergence of 5 parts in 10^{11}. The results obtained are reported in Figs. 1—5.

It can be seen from Figs. 2 and 3 that the use of $E_{1.5}$ rather than E_{UHF} in (3) gives only minor changes in the results. However the use of $\langle S^2 \rangle_{1.5}$ rather than $\langle S^2 \rangle_{\mathrm{UHF}}$ gives a more significant change, particularly for small values of α, that is for those values in which we are interested. This is because the use of $\langle S^2 \rangle_{1.5}$

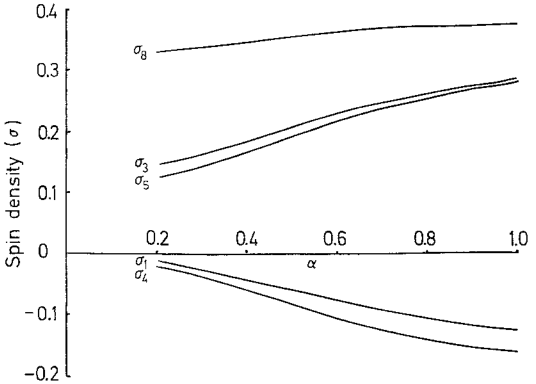

Fig. 6. Tropoloxyl. Variation of spin densites calculated from $A_{1.5}\,\psi_{\mathrm{UHF}}$ as a function of α where ψ_{UHF} is obtained by the minimisation of $\alpha E_{\mathrm{UHF}} + (1-\alpha)\langle S^2 \rangle_{\mathrm{UHF}}$

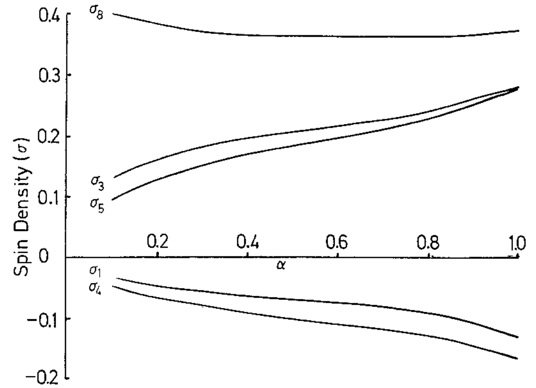

Fig. 7. Tropoloxyl. Variation of spin densities calculated from $A_{1.5}\,\psi_{\mathrm{UHF}}$ as a function of α where ψ_{UHF} is obtained by the minimisation of $\alpha E_{\mathrm{UHF}} + (1-\alpha)\langle S^2 \rangle_{1.5}$

does not restrict the contribution of the state with spin $s+1$, which is ultimately removed, while if $\langle S^2\rangle_{\mathrm{UHF}}$ is employed this contribution to Ψ is restricted. Thus the use of $\langle S^2\rangle_{1.5}$ in expression (3) allows the calculation more freedom and one would expect superior results.

The spin densities for the tropoloxyl radical are [8] $\sigma_5 = \pm 0.4$, σ_3 and σ_4 are equal to ± 0.27 and ± 0.1 using a Q value of 26 gauss [9], but definite assignments could not be made. From these calculations it seems that $\sigma_3 = +0.27$, $\sigma_4 = -0.1$ and $\sigma_5 = +0.4$ but quantitatively no value of α fits the experimental results very well (see Figs. 6 and 7). The use of a β_{CC} value of -1.0 eV for the pentadienyl radical calculation is physically unreal and the corresponding results are not given for this radical but it should be noted that the use of $\langle S^2\rangle_{1.5}$ gave results which differed markedly from those obtained using $\langle S^2\rangle_{\mathrm{UHF}}$.

In conclusion we suggest that Eq. (3) be used, (with a small value of α), for those cases in which the usual procedure results in a value of $\langle S^2\rangle$ which deviates considerably from $s(s+1)$. This would include those cases reported by Burnham [5]. Since the energy decreases with increasing α, it will be quite sufficient in many cases to use $\alpha = 1$, as has been the usual practice. However we feel that the analysis presented in this paper using Eq. (3) with $E = E_{\mathrm{UHF}}$ and $\langle S^2\rangle \equiv \langle S^2\rangle_{1.5}$ allows a much more careful study of the spin contaminants. In this way one is able to decide how large a deviation from $s(s+1)$ that one is going to tolerate in the value of $\langle S^2\rangle$ obtained. There seems no satisfactory general criterion for determining α in a given case. This arises from the fact that unless Ψ_{UHF} is completely projected, the application of incomplete projection operators, such as A_{s+1}, is a somewhat arbitrary procedure.

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