A SIMPLE WAY OF CALCULATION OF SPIN DENSITIES FROM RHF WAVE FUNCTION

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From study of non-stability of the RHF method a formula has been derived for addition of the spin-polarization component to the RHF spin densities. Spin densities of several radicals have been calculated by the INDO method. The results are compared with those of RHF CI and PUHF, the agreement being very good.

To obtain even qualitatively correct spin densities, the RHF method must be extended by configuration interaction or by perturbation method. Increasing number of electrons results in the problem of limitation of number of the used configurations and restriction of order of the perturbation method in the former and the latter method, respectively. Hence, although theoretical state of calculation of spin densities is clear in principle at present, it continues to be a topical problem to find a simple way giving not only a correct qualitative picture of spin distribution in a system but also the best possible quantitative results. Such proposal was recently submitted by Amos and coworkers[1] with the aim to improve the spin densities obtained from the UHF wave function. The aim of this communication is to suggest a simple method of correction of the 1. order to the spin densities obtained by the RHF method.

THEORETICAL

Studying non-stability of the RHF method, one of the authors (M. M. M.) arrived at the conclusion that the spin density matrix plays an important role in evaluation of external non-stability in the RHF method[2]. For introduction of the used symbolism and for better understanding of the derived relation we give a brief account of the basic ideas leading to the derived formalism.

It was shown[3] that the generalized version of HF method can be reduced to calculation of two matrixes Y and Z which represent (in restricted and unrestricted cases) matrices of residual charge densities and spin densities, respectively, and fulfil the following conditions:

$$[\mathbf{Y}, \mathbf{Z}]_+ = 0, \quad \mathbf{Y}^2 + \mathbf{Z}^2 = \mathbf{I}, \quad Sp\mathbf{Z} = 2M, \quad Sp\mathbf{Y} = N - m, \qquad (1)$$

where N, M, and m are number of electrons, spin projection value, and dimension of basic set, respectively. Variation of energy to the 1. order and conditions of the extreme are as it follows[3]:

$$\delta E = Sp(\mathbf{F}_1 \delta \mathbf{Y} + \mathbf{F}_2 \delta \mathbf{Z}) \tag{2}$$

$$[\mathbf{F}_1, \mathbf{Y}]_- + [\mathbf{F}_2, \mathbf{Z}]_- = 0, \quad [\mathbf{F}_1, \mathbf{Z}]_- + [\mathbf{F}_2, \mathbf{Y}]_- = 0 \tag{3}$$
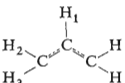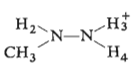
The ref.[3] gives discussion about the form of the operators $\mathbf{F}_1$ and $\mathbf{F}_2$ which are functions of $\mathbf{Y}$ and $\mathbf{Z}$ for the restricted and unrestricted HF method. In the restricted HF method a further condition must be fulfilled:

$$\mathbf{Z}^2 = \mathbf{Z}$$

and hence $\mathbf{Z} = \mathbf{I} - \mathbf{Y}^2$ and $\mathbf{Y}^3 = \mathbf{Y}$.

TABLE I

Spin Densities of Some Radicals Calculated by INDO Method in Two Parametrizations by RHF CI Method, and according to Eq. (9)

Radical	Atom	Pople[5]		Kaufman[6]	
		(9)	RTH CI	(9)	RTH CI
CH_3	H	—0·0215	—0·0278	—0·0326	—0·0414
C_2H_5	H_1	—0·0193	—0·0256	—0·0293	—0·0379
	H_2	0·0349	0·0463	0·0341	0·0475
HCO	H	0·1485	0·1990	0·1390	0·1817
$HC{=}CH_2$	H_1	0·0325	0·0347	0·0226	0·0190
	H_2 cis	0·0769	0·1304	0·0733	0·1269
	H_2 trans	0·0313	0·0443	0·0279	0·0405
NH_2	H	—0·0206	—0·0241	—0·0297	—0·0363
$\begin{smallmatrix} & H_1 & \\ H_2 & & H \\ C{-}C{-}C & \\ H_3 & & H \end{smallmatrix}$	H1	—0·00002	—0·0003	—0·00004	—0·0006
	H_2	—0·0103	—0·0130	—0·0157	—0·0197
	H_3	—0·0104	—0·0135	—0·0159	—0·0208
$CH_3NO_2^-$	H	0·0125	0·0135	0·0127	0·0135
$NH_2{-}NH_2^+$	H	—0·0133	—0·0171	—0·0189	—0·0245
$\begin{smallmatrix} H_2 & & H_3^+ \\ & N{-}N & \\ CH_3 & & H_4 \end{smallmatrix}$	$H_1(CH_3)$	0·0140	0·0149	0·0130	0·0131
	H_2	—0·0167	—0·0163	—0·0227	—0·0228
	H_3	—0·0082	—0·0087	—0·0129	—0·0137
	H_4	—0·0083	—0·0099	—0·0130	—0·0156

For calculation of the F_1 and F_2 operators we must know the matrix of the one-electron part of hamiltonian, the matrices K and G defined in ref.[3]

$$K_{pq}(Z) = -\tfrac{1}{2} \sum_{t,r} (pr \mid tq) Z_{tr} \qquad (4)$$

$$G_{pq}(Z) = \sum_{t,r} [(pr \mid qt) - \tfrac{1}{2}(pr \mid tq)] Z_{tr} \qquad (5)$$

and matrices Y and Z which, in the UHF and RHF schemes, are calculated according to Eq. (6)

$$Y = C_\alpha C_\alpha^+ + C_\beta C_\beta^+ - I$$
$$Z = C_\alpha C_\alpha^+ - C_\beta C_\beta^+ , \qquad (6)$$

where C_α and C_β are matrices of coefficients for the orbitals occupied by electrons with α and β spins, respectively. On the basis of the study of non-stability of the RHF method in ref.[2] the relation (7) was obtained for the energy variation to the first order for the RHF solution:

$$\delta E_0 = \tfrac{1}{2} Sp \, Y[YK(Z) \, Y - K(Z)] \, Y \delta Z , \qquad (7)$$

where δZ can be considered independent, and thus the choice:

$$\delta Z = -kY[YK(Z) \, Y - K(Z)] \, Y , \quad k > 0 \qquad (8)$$

ensures the inequality $\delta E_0 < 0$.

TABLE II
Analysis of Linear Dependence between Experimental *hfs* Constants and Spin Densities Calculated in INDO Approximation by RHF CI Method, PUHF Method and according to Eq. (9) in Two Parametrizations

Method	Number of points	Correlation coefficient	Standard deviation, mT	K_N mT
RHF CI[a]	17	0·991	0·55	65·51
(9)[b]	17	0·993	0·54	92·37
(9)[a]	17	0·996	0·45	86·21
PUHF[a]	17	0·996	0·47	—

Parametrization: [a] Kaufman[6], [b] Pople[5].

For the complete matrix of spin densities relation (9) is obtained from Eq. (8).

$$\varrho = \mathbf{Z} + \delta\mathbf{Z} \,. \tag{9}$$

Calculation Method

To enable comparison of the spin densities calculated from Eq. (9) with results of the RHF CI method, we chose the same set of radicals as that used for the reference RHF CI calculation[4] (Table I). The spin densities were calculated by the INDO method in standard parametrization[5] and in the parametrization suggested by Kaufman and coworkers[6].

RESULTS AND DISCUSSION

The relation (8) contains the constant k which must be determined additionally. It is the same for all matrices of spin densities and can be determined from the condition for the energy minimum in the given method.* In our case the calculation is a semiempirical one, the constant of proportionality between hfs constants and spin density

$$a_N = K_N \varrho_{sN} \tag{10}$$

being determined by the least squares method[5]. In our calculations it was presumed $k = 1$; additional comparison of the RHF CI results with our results shows that $k \sim 1$ (Table I). From Table I it follows that the spin densities calculated from Eq. (9) agree well with the values of the RHF CI method even without optimization of the k constant. As the calculation is semiempirical, Table II gives evaluation of the results by the least squares method. With the both parametrizations used the correlation coefficients are very good, being comparable with the best results of the UHF type calculation[4] and better than the RHF CI results. With respect to simple calculation this method can serve as a rapid and sufficiently accurate information source about spin distribution in open-shell systems.

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*   The problem of correct choice of the k constant will be discussed in a following *ab initio* calculation of spin densities using this method.