Theoret. Chim. Acta (Berl.) 52, 329–340 (1979)

THEORETICA CHIMICA ACTA
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Configuration Interaction Methods for Improving Unrestricted Hartree–Fock Spin Densities

A. Terry Amos
Department of Mathematics, The University, Nottingham, U.K.

Donald R. Beck
Theoretical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Ian L. Cooper
School of Chemistry, The University, Newcastle-upon-Tyne, U.K.

Limited Configuration Interaction wave functions based on Unrestricted Hartree–Fock natural orbitals are found to be easy to compute and to give much more satisfactory spin densities than are provided by techniques currently in use.

Key words: UHF spin densities, CI method for improving ~ – Spin densities, UHF ~

1. Introduction

There is a great need in quantum chemistry for a relatively simple yet reliable and reasonably accurate method of calculating spin densities in open-shell systems. For molecules of any size the most used method nowadays is the unrestricted Hartree–Fock (UHF) method which is fairly easy to implement but does have some drawbacks. In particular, since the UHF wave function is not an eigenfunction of the total spin operator, projection or annihilation procedures are necessary to produce meaningful spin densities [1–5]. While these spin densities are satisfactory enough for important chemical conclusions to be drawn (see, for example, the work of Claxton and his collaborators [6]; other references are given in the review by Thomson [7]) they are by no means as accurate as one would wish.

The purpose of this paper is to investigate a simple way of improving UHF spin densities by using a configuration interaction method with the natural UHF orbitals. This has been discussed implicitly by several authors ([4, 8, 9] for example) but most explicitly in a famous paper by Meyer [10]. It will be apparent that we have been much influenced by Meyer's work although we differ from him in two ways. Firstly, we use a straightforward configuration interaction approach rather than a perturbation procedure. Secondly, we apply the method in the context of pi

0040–5744/79/0052/0329/$02.40

electron theory. This enables us to side-step the basis-set problems endemic to *ab initio* calculations and has the advantage that, for a few molecules, we can compare our results with results which are exact within the pi electron model [11].

2. An Analysis of the UHF Wave Function

In the following we shall consider the UHF wave function and its improvement in the case of doublet states only. The application of the theory to other states with unpaired spins is obvious and entails no extra difficulties.

For a doublet state of a $2n + 1$ electron system the UHF wave function is a Slater determinant of $2n + 1$ orbitals:

$$\Psi_{\mathrm{UHF}} = A\{\mu_1\xi_1\mu_2\xi_2\cdots\mu_n\xi_n\mu_{n+1})(\alpha\beta\alpha\beta\cdots\alpha)\}, \tag{1}$$

where A is the antisymmetrizer. The orbitals in (1) are chosen to minimize the energy of Ψ_{UHF} and satisfy a set of equations similar to those of ordinary Hartree–Fock theory [12, 3].

It is always possible to choose the separate sets of α-spin and β-spin orbitals $\{\mu_i\}$ and $\{\xi_i\}$ to be orthogonal but, as a rule, there will be no orthogonality between sets. However, unitary transformations of the orbitals leave Ψ_{UHF} unchanged and this freedom can be used to obtain a new set of orbitals $\{\phi_i\}$, $\{\chi_i\}$ the corresponding orbitals [3, 13] with

$$\Psi_{\mathrm{UHF}} = A\{(\phi_1\chi_1\phi_2\chi_2\cdots\phi_n\chi_n\eta)(\alpha\beta\cdots\alpha)\} \tag{2}$$

and such that all the orbitals are normalized and orthogonal with the exception that

$$\langle\phi_i \mid \chi_j\rangle = T_i\delta_{ij}. \tag{3}$$

We choose the phases of the orbitals so that they are real and the T_i's are positive. This is purely a technical point but, as is emphasized by Phillips and Schug [14], unless some fixed choice of phase is made, inconsistencies can arise because of phase differences. The advantage of the choice we make is that the T_i are close to unity and for those exceptional cases where $T_i = 1$ then ϕ_i and χ_i are identical rather than differing by a phase factor.

In terms of the corresponding orbitals it is useful to define the natural orbitals (of charge). These are η and the $2n$ orbitals $\{\lambda_i\}$ and $\{\nu_i\}$ given by

$$\lambda_i = (2 + 2T_i)^{-1/2}(\phi_i + \chi_i); \qquad \nu_i = (2 - 2T_i)^{-1/2}(\phi_i - \chi_i). \tag{4}$$

For those special cases where $T_i = 1$ and, hence, $\phi_i = \chi_i$ we take $\nu_i = 0$.

As a practical point, we have found some difficulty in finding ν_i from Eq. (4) in those circumstances where T_i is close to unity due to severe loss of significant figures in the subtraction of nearly equal terms. To avoid this and to circumvent the use of the corresponding orbitals altogether, the natural orbitals can be found as eigenfunctions of the charge density matrix [2]:

$$\sum_{i=1}^{n+1} |\mu_i\rangle\langle\mu_i| + \sum_{i=1}^{n} |\xi_i\rangle\langle\xi_i|. \tag{5}$$

The paired orbitals λ_i and ν_i will be eigenfunctions of (5) with eigenvalues $1 + T_i$ and $1 - T_i$ respectively [2]; η will be associated with eigenvalue unity. As discussed by Phillips and Schug [14], in some cases there will be an eigenvalue equal to zero but the eigenfunctions associated with this can be ignored.

For the purpose of computing spin densities it is useful to introduce the natural orbitals of spin σ_0, $\{\sigma_i^+\}, \{\sigma_i^-\}$ $(i = 1 \cdots n)$. These are related to the natural orbitals by the following:

$$\sigma_0 = \eta; \qquad \sigma_i^{\pm} = (\lambda_i \pm \nu_i)/\sqrt{2}. \tag{6}$$

The inverse transformation of (6) is

$$\phi_i = A_i\lambda_i + B_i\nu_i, \qquad \chi_i = A_i\lambda_i - B_i\nu_i, \tag{7}$$

where

$$A_i = \tfrac{1}{2}(2 + 2T_i)^{1/2}, \qquad B_i = \tfrac{1}{2}(2 - 2T_i)^{1/2} \tag{8}$$

and these expressions allow Ψ_{UHF} to be analysed into various components (cf. [9, 4, 15]). Since the T_i are close to unity $A_i \approx 1$ and B_i is small. Consequently on substituting into (2) and ignoring terms which are third order in the B_i we find

$$\Psi_{\text{UHF}} = N\left\{\Psi_0 + \sum_{i=1}^{n} [A_i^{-1}B_i\tilde{\Psi}_i - A_i^{-2}B_i^2\Psi_{ii}] + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} A_i^{-1}A_j^{-1}B_iB_j\tilde{\Psi}_{ij}\right\}, \tag{9}$$

where N is a normalization factor and

$$\begin{aligned}
\Psi_0 &= A\{(\lambda_1\lambda_1\lambda_2\lambda_2\cdots\lambda_n\lambda_n\eta)(\alpha\beta\alpha\beta\cdots\alpha)\},\\
\tilde{\Psi}_i &= A\{(\cdots\nu_i\lambda_i\cdots\eta)(\cdots\alpha\beta\cdots\alpha + \cdots\beta\alpha\cdots\alpha)\},\\
\Psi_{ii} &= A\{(\cdots\nu_i\nu_i\cdots)(\cdots\alpha\beta\cdots)\},\\
\tilde{\Psi}_{ij} &= A\{(\cdots\nu_i\lambda_i\cdots\nu_j\lambda_j\cdots)(\cdots\alpha\beta\cdots\alpha\beta\cdots + \cdots\alpha\beta\cdots\beta\alpha\\
&\qquad + \beta\alpha\cdots\beta\alpha\cdots + \cdots\beta\alpha\cdots\alpha\beta\cdots)\}.
\end{aligned}$$

It is well known that Ψ_{UHF} is not a pure spin state and this is shown explicitly in (9) since, while Ψ_0 and Ψ_{ii} are doublets, $\tilde{\Psi}_i$ is a mixture of doublet and quartet and $\tilde{\Psi}_{ii}$ is a mixture of doublet, quartet, and sextet. We can remove the unwanted quartet and sextet components from Ψ_{UHF} by applying the annihilation operator

$$(S^2 - 15/4)(S^2 - 35/4)/24, \tag{10}$$

which leaves unchanged any part of Ψ_{UHF} that is already a doublet. As a consequence the new wave function becomes

$$\begin{aligned}
\Psi_A = N'\Big\{\Psi_0 &+ \sum_i [\sqrt{\tfrac{2}{3}}A_i^{-1}B_i\Psi_i - A_i^{-2}B_i^2\Psi_{ii}]\\
&+ \sum_{i<j} \sqrt{\tfrac{4}{3}}A_i^{-1}A_j^{-1}B_iB_j\Psi_{ij}\Big\} + O(B^3),
\end{aligned} \tag{11}$$

where Ψ_i and Ψ_{ij} are the normalized doublet components of $\tilde{\Psi}_j$ and $\tilde{\Psi}_{ij}$. Their explicit forms, in an abbreviated notation, are:

$$\begin{aligned}
\Psi_i &= 6^{-1/2}A\{(\nu_i\lambda_i\eta)(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)\},\\
\Psi_{ij} &= 12^{-1/2}A\{(\nu_i\lambda_i\nu_j\lambda_j)(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha - 2\beta\beta\alpha\alpha - 2\alpha\alpha\beta\beta)\}.
\end{aligned} \tag{12}$$

For what follows, it is convenient to rewrite (11) with variable coefficients for the various terms, giving a wave function

$$\Psi_c = a_0\Psi_0 + \sum [b_i\Psi_i + c_i\Psi_{ii}] + \sum_{i<j} d_{ij}\Psi_{ij}. \tag{13}$$

Assuming real wave functions and coefficients, Ψ_c will be normalized if

$$a_0^2 + \sum \{b_i^2 + c_i^2\} + \sum_{i<j} d_{ij}^2 = 1. \tag{14}$$

3. Spin Densities

The most important use of the UHF method is to calculate spin densities. As a rule this is done by applying that part of annihilator (10) which removes the quartet component and evaluating the spin density ρ as

$$\begin{aligned}\rho = \langle\tfrac{1}{3}(S^2 - 15/4)\Psi_{\text{UHF}}|\boldsymbol{\rho}|\tfrac{1}{3}(S^2 - 15/4)\Psi_{\text{UHF}}\rangle/\\ \langle\tfrac{1}{3}(S^2 - 15/4)\Psi_{\text{UHF}} \mid \tfrac{1}{3}(S^2 - 15/4)\Psi_{\text{UHF}}\rangle,\end{aligned} \tag{15}$$

where $\boldsymbol{\rho}$ is the spin-density operator. While this gives satisfactory results in many cases it does suffer from the disadvantage that the wave function used is not a pure spin state since there remain unwanted sextet and higher components. When the weights of these components are large or equal in magnitude to the weight of the quartet component in Ψ_{UHF} then (15) can give misleading results.

One way to avoid this is to apply the full projection operator to Ψ_{UHF} and use the formulae of Harriman [2]. An alternative is to use the pure spin state Ψ_c and evaluate

$$\rho = \langle\Psi_c|\boldsymbol{\rho}|\Psi_c\rangle/\langle\Psi_c \mid \Psi_c\rangle. \tag{16}$$

In both cases it turns out that ρ can be written in terms of the natural orbitals of spin (Eq. 6):

$$\rho = e(\sigma_0)^2 + \sum_i \{f_i^+(\sigma_i^+)^2 - f_i^-(\sigma_i^-)^2\}, \tag{17}$$

where the constants e, $\{f_i^\pm\}$ are occupation numbers. When (16) is used the occupation numbers are given by

$$\begin{aligned}e &= 1 - \tfrac{4}{3}\sum_i b_i^2,\\ f_i^\pm &= \sqrt{\tfrac{2}{3}}a_0b_i \pm \tfrac{2}{3}b_i^2 - \sqrt{\tfrac{2}{3}}b_ic_i + \tfrac{1}{3}\sqrt{2}\left\{\sum_{j=1}^{i-1} b_jd_{ji} + \sum_{j=i+1}^{n} b_jd_{ij}\right\}.\end{aligned} \tag{18}$$

If the full projection operator is used (18) will give the leading terms in the occupation numbers formulae.

Equation (18) makes clear the important role played by the parameters $\{b_i\}$ in determining the spin densities: in order to get satisfactory values for ρ correct order of magnitude estimates of the b_i's must be obtained. Unfortunately the b_i's [i.e., $NA_i^{-1}B_i$, cf. Eq. (9)] given by the UHF method tend to be much too small. This is

Table 1. Values of b_1, c_1, occupation numbers and spin densities in allyl obtained from various wave functions

			Occupational numbers			Spin densities	
Wave function	b_1	$-c_1$	e	f_1^+	f_1^-	End Atom	Central Atom
Projected UHF	0.125	0.024	0.979	0.114	0.093	0.547	−0.093
EHF [2, 16]	0.238	0.088	0.924	0.242	0.167	0.584	−0.167
Variational	0.210	0.112	0.941	0.215	0.156	0.578	−0.156
Complete CI [11]	—	—	—	—	—	0.578	−0.156

most easily demonstrated by a pi electron calculation on the allyl radical. In Table 1 we compare the UHF value of b_1 and c_1 ($n = 1$ for allyl) with variationally determined values. Also in Table 1 we give occupation numbers and spin densities at the end and central atom. The table makes clear that the poor values of b_1 and c_1 given by the UHF method lead to inaccurate values for the spin densities.

It has often been argued that the UHF method is unsatisfactory because the orbitals, and, hence, the natural orbitals and occupation numbers are determined by applying the variational method to (1) whereas it ought to be applied to the doublet component of Ψ_{UHF} only. If this is done we have the extended Hartree–Fock (EHF) method which is more difficult to implement although in recent years quite a number of EHF calculations have been reported (for example, [2] and [16]). Normally the EHF and UHF natural orbitals will differ but for allyl symmetry causes them to be equal. Thus, for allyl, EHF values of b_1 and c_1 can be compared directly with UHF and variationally determined values. When this is done in Table 1 it can be seen that the EHF method gives better results than the UHF method because the b_1 (in effect the B_1) value is much larger. However there is an overcompensation and the EHF spin densities do differ from the exact ones. In fact Table 1 rather overstates the case for EHF spin densities. In two other radicals pentadienyl and benzyl, where complete CI spin densities (these are, of course, "exact" within the context of pi electron theory) are available there is not good agreement with EHF values.

We believe that these errors in UHF and EHF spin densities are due to the strong constraints placed on the various terms in the wave functions. Thus, on comparing (11) with (13), we see that, in terms of the parameters $\{A_i, B_i\}$, in both UHF and EHF methods the weights of Ψ_i, Ψ_{ii}, Ψ_{ij} are

$$b_i = \sqrt{\tfrac{2}{3}}A_i^{-1}B_i; \quad c_i = -A_i^{-2}B_i^2 = -\tfrac{3}{2}b_i^2; \quad d_{ij} = \sqrt{\tfrac{4}{3}}A_i^{-1}A_j^{-1}B_iB_j = \sqrt{3}b_ib_j. \tag{19}$$

In allyl the variational value of b_1 is such that $-\frac{3}{2}(b_1)^2 = -0.066$ which does not agree with the variational value of $c_1 = -0.112$. By imposing the constraints (19), the EHF B_1 value is made too large to give a good estimate of b_1 because it simultaneously is attempting to give a reasonable estimate of c_1; that is to say imposing the constraints distorts the wave function away from its most satisfactory form. We conclude that a promising method for improving on the UHF and EHF wave functions is to allow for free, unconstrained variation of the coefficients b_i, c_i and d_{ij} in (13). This is equivalent to a limited configuration interaction method for computing spin densities.

4. Configuration Interaction Methods

It has long been realized that the CI method provides a means of calculating spin densities (for early work see [16, 17]). Unfortunately it is difficult to know exactly what configurations to include in the wave function. On the other hand the analysis of the previous two sections shows that the UHF and EHF wave functions themselves can be considered as CI wave functions with a rather restricted set of configurations and with certain imposed relations between the coefficients of the various configurations.

The obvious extension of this is to perform an ordinary CI calculation with these same configurations and Meyer [10] has, in effect, suggested this approach which is implicit also in the work of Nakatsuji (see [18], in particular). Unfortunately both these authors adopt a type of perturbation theory which makes their results difficult to interpret. Moreover, in Meyer's work, the theory is applied in an *ab initio* context, using a basis set of Gaussian orbitals. Thus it is not easy to evaluate his results because of the difficulty of distinguishing between effects due to the basis set and those due to his method of approach.

There is, therefore, an advantage to be gained by finding CI wave functions of the type Ψ_c given in (13) for pi systems where there are no basis set problems and where all configurations of the appropriate form can be included. What is more, for some small pi-electron systems complete CI results are available for comparison [11].

When adopting this approach there are three points which can be considered. These are: (1) the possible further reduction of the number of configurations in the wave function, (2) the best choice of orbitals, and (3) empirical schemes to simplify the calculations. We now discuss these in turn.

4.1 Number and Types of Configurations

For a $(2n + 1)$ electron system, as well as Ψ_0, Ψ_c consists of n singly-excited configurations $\{\Psi_i\}$, n doubly-excited configurations $\{\Psi_{ii}\}$, and $\frac{1}{2}(n^2 - n)$ doubly-excited configurations $\{\Psi_{ij}\}$ giving $1 + \frac{3}{2}n + \frac{1}{2}n^2$ terms in all. The n^2 dependence arises from the Ψ_{ij} terms which are the most difficult to deal with from the point of view of evaluating the matrix elements required for the secular matrix. Therefore we have investigated whether these can be neglected. In addition, since there are in the literature quite a number of CI calculations of spin densities which have used singly-excited configurations only (e.g. [17] and [19]), we have examined whether a wave function built up only of Ψ_0 and the $\{\Psi_i\}$ terms can give acceptable results.

Table 2. Spin densities in benzyl obtained from various CI wave functions

Wave function and configurations included	Energy (eV)	Spin densities at atom[a]				
		1	2	3	4	7
Simplest case: Ψ_0, Ψ_i	-132.32	-0.087	0.172	-0.064	0.160	0.709
Limited case Ψ_L: $\Psi_0, \Psi_i, \Psi_{ii}$	-132.53	-0.095	0.179	-0.070	0.167	0.711
Ψ_c: $\Psi_0, \Psi_i, \Psi_{ii}, \Psi_{ij}$	-132.67	-0.109	0.195	-0.087	0.177	0.716
Approximate Ψ_c	—	-0.110	0.195	-0.087	0.178	0.716
EHF [16]	-132.71	-0.134	0.279	-0.143	0.260	0.602
Complete CI [11]	—	-0.110	0.185	-0.070	0.165	0.715

[a] In this and following tables the numbering of the atoms is that given in Refs. [2] and [4].

The results for benzyl spin densities are given in the first three rows of Table 2. Three cases are considered: in the simplest only singly-excited configurations are included, i.e. we take $c_i = d_{ij} = 0$; we refer to the situation where the double excitations Ψ_{ii} are included but not the Ψ_{ij} (i.e. $d_{ij} = 0$) as the limited CI and denote the wave function as Ψ_L; the third case corresponds to the wave function Ψ_c (however, for simplicity, matrix elements between different Ψ_{ij} configurations are ignored).

A comparison of the spin densities given by these three methods with those given by a complete CI calculation suggests the following:

(1) It is not sufficiently accurate to include single-excitations only. This agrees with the results found by Meyer [10].

(2) Very acceptable spin densities are given by the limited CI wave function, i.e. that made up of Ψ_0 and the $\{\Psi_i\}$ and $\{\Psi_{ii}\}$ $(i = 1 \cdots n)$.

(3) Inclusion of the $\{\Psi_{ij}\}$ configurations does not improve the spin densities and, on the whole, makes them worse. In this respect benzyl is somewhat atypical of the molecules we have considered. For the other molecules, the addition of the $\{\Psi_{ij}\}$ terms makes very little difference to the spin densities.

(4) With regard to the energies associated with the different wave functions it is, of course, the case that including more configurations lowers the energy. However, none of these CI wave functions gives as good an energy as the EHF method.

4.2. Choice of Orbitals

The above results and analysis are based on the assumption that the most suitable orbitals to use are the UHF natural orbitals. But, of course, within the CI method it is quite feasible to use other orbitals. For example, Hinchliffe [17] has used restricted Hartree–Fock (RHF) orbitals (i.e. those which minimize the energy of Ψ_0) and Claxton and Weiner [19] have used MCSCF orbitals which minimize the energy of their CI wave function. In both cases, however, the CI wave function contained single excitations only.

We have examined whether or not some of these other orbitals can improve the limited CI wave function Ψ_L (i.e. Ψ_c excluding the Ψ_{ij} terms) for the case of the

Table 3. Spin densities and energies for pentadienyl obtained using different orbital types

y	Orbital type	Spin densities at atom[a]			Energy (eV)
		1	2	3	
0.504	RHF	0.369	−0.126	0.513	−63.606
0.553	UHF	0.419	−0.131	0.424	−63.666
0.567	MCSCF	0.434	−0.131	0.396	−63.670
0.570	EHF	0.437	−0.132	0.390	−63.670

[a] The spin densities given by a complete CI calculation are 0.413, −0.140, 0.452.

pentadienyl radical. The choice of pentadienyl is dictated by the fact that the orbitals are determined mostly by symmetry. Thus we take

$$\begin{aligned} \left.\begin{matrix}\lambda_1\\ \nu_1\end{matrix}\right\} &= (\tfrac{1}{4} - \tfrac{1}{2}y^2)^{1/2}(\omega_1 + \omega_5) + y\omega_3 \pm \tfrac{1}{2}(\omega_2 + \omega_4) \\ \left.\begin{matrix}\lambda_2\\ \nu_2\end{matrix}\right\} &= \tfrac{1}{2}(\omega_1 - \omega_5) \pm \tfrac{1}{2}(\omega_2 - \omega_4) \\ \eta &= y(\omega_1 + \omega_5) - (1 - 2y^2)^{1/2}\omega_3 \end{aligned} \tag{20}$$

where the $\{\omega_i\}$ are basis orbitals. Different values of the parameter y will give different types of orbitals. As well as RHF and UHF natural orbitals we consider EHF natural orbitals and MCSCF orbitals. The results for spin densities and energies are given in Table 3.

These results for pentadienyl are rather disturbing. Orbitals which differ only marginally (i.e. are given by (20) with only slightly different y values, cf. Table 3) can give spin densities which differ considerably. The UHF natural orbitals produce spin densities in best agreement with the complete CI spin densities but the EHF natural orbitals are better from an energy point of view. It is noteworthy that the EHF natural orbitals are almost the same as the energetically optimum ones, i.e. the MCSCF orbitals.

The RHF orbitals give rather poor results both for spin densities and for the energy. This is rather surprising for there are plausible reasons for favouring these orbitals. The limited CI function Ψ_L does not include all possible singly-excited configurations by any means; for example, $\lambda_i \rightarrow \nu_j$ and $\eta \rightarrow \nu_j$ are excluded. With RHF orbitals the matrix elements of the Hamiltonian between these configurations and Ψ_0 will be zero and so, on perturbation-theoretic grounds, it can be argued that such configurations need not be included since, even if they were, their weights would be very small indeed. The same matrix elements are non-zero if other orbitals are used and so if these other singly-excited configurations were included, as ideally they should be, then large and more significant changes might be expected.

We have examined this point of view in the case of pentadienyl by adding in the extra singly-excited configuration $\eta \rightarrow \nu_1$. It is certainly true that the matrix element between this and Ψ_0 is zero when RHF orbitals are used and is non-zero, though not especially large, when UHF or EHF natural orbitals are used. However, other matrix elements involving the extra configuration and the configurations Ψ_i and Ψ_{ii} do not vanish for RHF orbitals and the effect of these lead to results which are contrary to what is expected. For RHF orbitals the inclusion of the $\eta \rightarrow \nu_1$ term causes considerable changes in the weights of the original configurations in Ψ_L with consequent changes in the spin densities. With UHF or EHF natural orbitals, on the other hand, there appears to be considerable cancellation so that the configuration weights and spin densities are hardly changed when the extra term is included.

Our conclusion, therefore, is that UHF and EHF natural orbitals are more satisfactory than RHF orbitals in forming Ψ_L. From the point of view of finding spin densities the UHF orbitals are better but the contrary is true if energies are to be determined. Even if energies are required, however, the advantage of the EHF orbitals is rather marginal and, of course, they are much more difficult to calculate.

4.3. *Empirical Methods*

In a previous note [15] we have suggested an empirical method for improving UHF spin densities. This amounts to using a wave function of the form given in Eq. (11) (but without the cross terms) with the $A_i^{-1}B_i$ values taken to be those given in a UHF calculation and scaled upwards by a factor of 5/3, that being the value appropriate for allyl and empirically assumed to apply to all molecules. This is equivalent to using Ψ_L and assuming that the weights of the configurations are given by:

$$\begin{aligned} b_i/a_0 &= \tfrac{5}{3}\sqrt{\tfrac{2}{3}}G_i \\ c_i/a_0 &= -\tfrac{25}{9}G_1^2 \end{aligned} \tag{21}$$

where

$$G_i = [(1 - T_i)/(1 + T_i)]^{1/2}.$$

In Table 4 we compare these empirical values with the variational values in the case of benzyl. We also give the values given by the UHF wave function, i.e. without the scaling factor. On the whole the scaling does lead to better values although the estimates for the b_i/a_0 are too large and those for c_i/a_0 too small. As explained earlier this is a consequence of the constraints involved in any wave function of UHF or EHF type.

In a similar vein it is possible to begin with the limited CI wave function Ψ_L and to attempt to convert it into a Ψ_c wave function by adding the Ψ_{ij} configurations empirically. This can be done by assuming the d_{ij} coefficients are related to the c_i and c_j coefficients by the empirical relationship

$$d_{ij} = \sqrt{(4c_ic_j/3)} \tag{22}$$

Table 4. Variational, empirical and UHF values for configuration weights in a limited CI wave function for benzyl

Configuration weights	Variational value	Empirical (scaled UHF)	Unscaled UHF
b_1/a_0	0.055	0.068	0.041
b_2/a_0	0.100	0.144	0.086
b_3/a_0	0.155	0.160	0.096
$-c_1/a_0$	0.021	0.007	0.002
$-c_2/a_0$	0.108	0.031	0.011
$-c_3/a_0$	0.077	0.039	0.014

which is that relationship holding in Eq. (19) and in UHF and EHF wave functions. This gives an approximate Ψ_c and the spin densities obtained from it can be compared with those obtained from the exact Ψ_c for the case of benzyl in Table 2. The agreement is excellent and we have found similar agreement for the other molecules we have considered. Thus it is sufficient to perform the CI calculations with the limited configurations; the extra Ψ_{ij} configurations can be included, if desired, by the above empirical device.

5. Results

We have used the methods described in the previous sections to compute spin densities in a number of hydrocarbon radicals and positive ions. The choice of molecules was made to obtain a representative sample and tend to be those for which other values are available for comparison. The UHF orbitals were obtained by iterating the UHFSCF equations until the orbitals were changing in the sixth decimal place. As a check on convergence the UHF spin densities were compared with those of Claxton and McWilliams [20] and agreed in every case. For each molecule we have computed the limited CI wave function Ψ_L, the approximate Ψ_c and the empirical Ψ_L, these last two as described in Sect. 4.3. The spin densities obtained from these wave functions are listed in Table 5. For comparison we include also UHF spin densities after annihilation [4, 14], EHF spin densities [2] and the SCFCI and MCSCF results of Claxton and Weiner [19] based on CI wave functions which contained some singly-excited configurations only. Finally we have given the complete CI spin densities for those molecules where values are available.

The conclusions we would wish to draw from Table 5 can be stated very briefly. The limited CI wave function gives spin densities which, in most cases, are in very good agreement with the complete CI values. For pentadienyl and benzyl the spin densities are less satisfactory but even so the use of Ψ_L leads to better values than any other method. As a rule the limited CI results lie between the UHF and EHF ones.

With regard to the approximate and empirical methods we see that they produce results in broad agreement with those of the limited CI method. In particular the empirical Ψ_L wave function, obtained by scaling the B_i values obtained for the UHF wave function, seems to provide a quick and easy way to find spin densities.

Table 5. Spin densities computed by various methods

Molecule	Atom	UHF	SCFCI	MCSCF	EHF	Complete CI	Ψ_L	Approx. Ψ_c	Empirical [a]Ψ_L
Allyl	1	0.547	—	—	0.584	0.578	0.578	—	0.574
	2	−0.093	—	—	−0.167	−0.156	−0.156	—	−0.147
Pentadienyl	1	0.387	0.354	0.378	0.452	0.413	0.419	0.433	0.435
	2	−0.096	−0.112	−0.113	−0.159	−0.140	−0.131	−0.144	−0.144
	3	0.418	0.515	0.471	0.415	0.452	0.424	0.421	0.417
Benzyl	1	−0.062	−0.081	−0.085	−0.134	−0.110	−0.095	−0.110	−0.096
	2	0.163	0.141	0.157	0.279	0.185	0.179	0.195	0.198
	3	−0.054	−0.048	−0.051	−0.143	−0.070	−0.070	−0.087	−0.084
	4	0.134	0.104	0.106	0.260	0.165	0.167	0.178	0.170
	7	0.711	0.790	0.767	0.602	0.715	0.711	0.716	0.699
Butadiene[a]	1	0.389	—	—	—	0.411	0.413	—	0.410
	2	0.111	—	—	—	0.089	0.087	—	0.090
Naphthalene[a]	1	0.215	0.230	0.231	0.252	—	0.236	0.235	0.228
	2	0.048	0.043	0.042	0.027	—	0.038	0.039	0.041
	9	−0.024	−0.046	−0.046	−0.059	—	−0.047	−0.047	−0.039
Anthracene[a]	1	0.105	—	—	0.138	—	0.119	0.117	0.115
	2	0.028	—	—	0.014	—	0.023	0.024	0.024
	9	0.260	—	—	0.293	—	0.283	0.281	0.276
	11	−0.014	—	—	−0.048	—	−0.033	−0.032	−0.027

[a] These differ from the results given in Ref. [15] since here the complete spin density expression was used with fully converged UHF orbitals.

Our main conclusion, therefore, is that, at least in the context of pi electron theory, the use of the limited CI wave function based on UHF natural orbitals provides a simple, reliable and reasonably accurate method of calculating spin densities in open-shell systems.

Acknowledgments. We wish to thank the NATO Research Grants Programme for financial support for this work.

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Received January 30, 1979