An Unrestricted Hartree-Fock Self-consistent Hückel-like Procedure. Application to the Magnetic Properties of Radicals and Metallic Clusters

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The Hückel method, which can be considered an SCF method on the orthogonalized Löwdin basis, is extended to the UHF model. Some applications to π-radicals and to metallic clusters are given. A strong magnetization can appear, even in small size clusters. Correlation with the Hund rule is discussed. A calculation carried out on a tetrahedral cluster explains the origin of the strong magnetization in elements located in the middle of the transition elements period. Examples of antiferro- and ferrimagnetic clusters are given.

INTRODUCTION

The self-consistent field (SCF) method[1] is certainly, at the present time, the best procedure for studying molecular systems. Nevertheless, the complexity and size of the numerical calculations involved in this method make its application difficult and very expensive when the system exceeds a certain size. Therefore, not only do earlier empirical methods continue to be utilized, but new empirical or semiempirical methods have also been proposed. Owing to the fact that the larger the system is, the simpler the procedure must be in order to be applicable, in extreme cases, the only procedure which remains practicable is the one devised fifty years ago by Hückel, Hund and Mulliken — usually known as the Hückel method.

This method is often considered as an empirical model owing to the simplifying hypothesis on which it is built. Therefore, all the possibilities of this method have not been utilized. In particular, its adaptation to the unrestricted Hartree-Fock model has never been attempted. Such an adaptation should allow a consideration of the problem of magnetic properties in metallic clusters, generally investigated in terms of the Hubbard model[2] or more recently by means of the X_α — method[3] (SCF simplified procedure).

Before describing this extension of the classical Hückel method, it is necessary to recall the theoretical status of this method as a simulated SCF procedure[4].

THE THEORY

Notations and Classical SCF Results

Let us consider a 2n-electrons system. Generally, it is possible to describe the ground state by means of a single Slater determinant biult up on molecular

orbitals φ_i successively multiplied by each of the spin-functions α or β:

$$\psi = \det | \ldots \varphi_i\alpha, \varphi_i\beta, \ldots | \qquad (i = 1 \text{ to } n) \qquad (1)$$

(the φ_i's being orthonormal). This structure is called the restricted Hartree-Fock model (RHF).

The electronic Hamiltonian operator can be written;

$$\hat{H} = \sum_\mu \hat{I}(\mu) + \sum_{(\mu\nu)} \frac{1}{r_{\mu\nu}} \qquad (2)$$

$\hat{I}$ being a monoelectron operator (kinetic energy + attraction energy between the nuclei or the cores, and the electron μ).

If we developp the φ_i molecular orbitals on the χ_p atomic orbitals:

$$\varphi_i = \sum_p c_{ip} \chi_p \qquad (3)$$

the total electron energy is[5]:

$$E_e = \sum_{i=1}^n (I_i + e_i) \qquad (4)$$

where:

$$I_i = \langle \varphi_i \hat{I} \varphi_i \rangle \qquad (5)$$

and where e_i is the root of the secular equation

$$\det | F_{pq} - e\, S_{pq} | = 0 \qquad (6)$$

corresponding to the φ_i orbital.

$$\begin{cases} S_{pq} = \langle \chi_p \chi_q \rangle \text{ (overlap integral)} \\ F_{pq} = I_{pq} + G_{pq} \end{cases} \qquad (7)$$

$$= \langle \chi_p \hat{I} \chi_q \rangle + \sum_{j=1}^n \sum_r \sum_s c_{jr}c_{js} [2\,(pq, rs) - (ps, rq)]$$

$$\text{with } (pq, rs) = \langle \chi_p(\mu) \chi_q(\mu) \frac{1}{r_{\mu\nu}} \chi_r(\varkappa) \chi_s(\varkappa) \rangle \qquad (8)$$

The terms I_{pq} (7) can be explicited as functions of the energies W_q of the electrons in the corresponding atom cores Q^{+q}, and the (R^{+r}, pq) integrals, corresponding to the interaction between the R^{+r} core and the electron density pq:

$$I_{pq} = W_q S_{pq} + \sum_{R \neq Q} (R^{+r}, pq)$$

$$= W_q S_{pq} - \sum_{r \neq q} n_r\,(rr, pq) + \sum_{R \neq Q} (R, pq) \qquad (9)$$

where n_r = positive charge of the core R^{+r},

R = potential created by the neutral atom R.

If we replace the basis atom orbitals χ, generally not orthogonal, by orthogonalized atom orbitals χ' obtained by the Löwdin procedure[6], the new bielectronic integrals (8) are practically equal to zero, except for $p = q$ and $r = s$; in this case, they are equal to the initial corresponding integrals:

$$(p'q', r's') \sim (pq, rs)\, \delta_{pq}\, \delta_{rs} \qquad (10)$$

If we neglect the S^2 terms, the charges of the atomic orbitals are respectively equal in both bases:

$$q'_r \sim q_r \tag{11}$$

In the orthogonalized basis (χ'), the charge expression is the following:

$$q'_r = 2 \sum_{i=1}^{n} c_{ir}^2 \tag{12}$$

Under these conditions, the expressions (7) are simplified. They become:

$$\begin{cases} G_{pp} = \dfrac{1}{2} q_p C_{pp} + \sum_{q \neq p} q_q C_{pq} \\[2mm] G_{pq} = -\dfrac{1}{2} l_{pq} C_{pq} \end{cases} \tag{13}$$

with:

$$C_{pq} = (pp, qq) \text{ and } l_{pq} = 2 \sum_i c_{ip} c_{iq} \text{ (bond order)} \tag{14}$$

In the orthogonalized basis, the secular equation (6) becomes:

$$\det \left| L_{pq} - e\, \delta_{pq} \right| = 0 \tag{15}$$

where:

$$L_{pp} = W_p + \frac{1}{2} q_p C_{pp} + \sum_{r \neq p} (q_r - n_r) C_{pr} + \sum_{R \neq P} (R, pp) \tag{16}$$

In this expression, we can neglect the (R, pp) terms because these terms are small and because the value of the summation is practically the same for all the atoms P. Consequently, if the values of the net charges $(n_r - q_r)$ are equal to zero or are very small, we obtain:

$$L_{pp} \sim W_p + \frac{1}{2} n_p C_{pp} \tag{17}$$

Consequently, the diagonal elements L_{pp} do not depend on the molecule, they depend practically only on the nature of the corresponding atomic orbital. These elements are transferable from one molecule to another. In order to conform to usage we shall write:

$$L_{pp} = \alpha_p \tag{18}$$

Likewise, it is possible to show that the off-diagonal elements

$$L_{pq} = I_{pq} - \frac{1}{2} l_{pq} C_{pq} \tag{19}$$

depend practically only on the nature of the χ_p and χ_q orbitals, and on their respective positions. These terms are also transferable. They are equal to zero if the P and Q atoms are not bonded. If $L_{pq} \neq 0$, we shall write:

$$L_{pq} = \beta_{pq} \tag{20}$$

The electron energy (3) becomes[7]:

$$E_{RHF} = 2 \sum_i e_i - \frac{1}{4} \sum_p q_p^2 C_{pp} + \frac{1}{2} \sum_{(pq)} l_{pq}^2 C_{pq} - \sum_{(pq)} q_p q_q C_{pq} \tag{21}$$

In conclusion, we see that the transferability of the Fock-matrix elements in the orthogonalized basis allows us to write directly the secular equation (15), and to obtain the orbital energies e_i and the molecular orbitals φ_i with good accuracy. We have rediscovered the old Hückel method. But the expression of the electron energy is more complicated than in the Hückel method ($E_{Hü} = 2 \sum_i e_i$).

Generalization to the UHF Procedure

If the number of the electrons is odd, or if the system has degenerated levels, each molecular orbital φ_i cannot be used twice. In these cases, we have two possibilities. At first, we can keep the Hartree-Fock model with twice utilized molecular orbitals and singly utilized orbitals. The second possibility is the unrestricted Hartree-Fock procedure (UHF), where all the space-functions are different. In this case, the functions φ corresponding to the same spin--function (α or β) are orthogonal, but no relation exists between the two φ functions corresponding to different spin-functions. The orthogonality is automatically obtained owing to the spin-functions orthogonality. For example:

$$\psi = |\; \varphi_1 \alpha, \varphi_3 \alpha, \; \dots \; \varphi_a \alpha, \varphi_2 \beta, \varphi_4 \beta, \; \dots \; \varphi_b \beta \;| \tag{22}$$

The principle of the general treatment is well known[8]. It is necessary to make alternative iterations on the two matrices F^{α}_{pq} and F^{β}_{pq}, corresponding respectively to the two molecular orbitals families.

In order to avoid confusions between the Hückel parameters α and β (18, 20), and the spin-functions, we shall note subsequently the latter functions by means of the symbols ↑ (up) for the α functions, and ↓ (down) for the β functions.

For the ↑ family, for example, we have:

$$F\!\uparrow_{pq} = I_{pq} + G\!\uparrow_{pq} \tag{23}$$

with:

$$G\!\uparrow_{pq} = \Sigma\!\uparrow_i \; \Sigma_r \; \Sigma_s \; c\!\uparrow_{ir} c\!\uparrow_{is} (pq, rs) + \Sigma\!\downarrow_j \; \Sigma_r \; \Sigma_s \; c\!\downarrow_{jr} c\!\downarrow_{js} (pq, rs) - \Sigma\!\uparrow_i \; \Sigma_r \; \Sigma_s \; c\!\uparrow_{ir} c\!\uparrow_{is} (pq, rs) \tag{24}$$

where $i = 1, 3, \dots$ a, and $j = 2, 4, \dots$ b. The superior indices (↑ or ↓) indicate the family to which the corresponding molecular orbitals belong.

In the Löwdin basis, the expressions (24) become:

$$G\!\uparrow_{pq} = - \; \Sigma\!\uparrow_i \; c\!\uparrow_{ip} \, c\!\uparrow_{iq} \, C_{pq} = - l\!\uparrow_{pq} \, C_{pq} \tag{25}$$

with:

$$l\!\uparrow_{pq} = \Sigma\!\uparrow_i \; c\!\uparrow_{ip} \, c\!\uparrow_{iq} \tag{26}$$

and

$$G\!\uparrow_{pp} = \Sigma\!\uparrow_i \; \Sigma_r \; (c\!\uparrow_{ir})^2 \, C_{pr} + \Sigma\!\downarrow_j \; \Sigma_r \; (c\!\downarrow_{jr})^2 \, C_{pr} - \Sigma\!\uparrow_i \; \Sigma_r \; (c\!\uparrow_{ir})^2 \, (pr, pr)$$

$$= \Sigma\!\downarrow_j \; (c\!\downarrow_{jp})^2 \, C_{pp} + \Sigma_r \; C_{pr} \, [\Sigma\!\uparrow_i \; (c\!\uparrow_{ir})^2 + \Sigma\!\downarrow_j \; (c\!\downarrow_{jr})^2] = q\!\downarrow_p \, C_{pp} + \sum_{r \neq p} q_r \, C_{pr} \tag{27}$$

with:

$$q\!\uparrow_p = \Sigma\!\uparrow_i \; (c\!\uparrow_{ip})^2; \quad q\!\downarrow_p = \Sigma\!\downarrow_j \; (c\!\downarrow_{jp})^2 \quad \text{and} \quad q_p = q\!\uparrow_p + q\!\downarrow_p \tag{28}$$

Consequently, if we neglect the (R, pp) terms:

$$L\uparrow_{pp} = W_p + q\downarrow_p C_{pp} + \sum_{r \neq p} (q_r - n_r) C_{pr}$$

$$= (W_p + \frac{1}{2} n_p C_{pp}) + (q\downarrow_p - \frac{1}{2} n_p C_{pp}) + \sum_{r \neq p} (q_r - n_r) C_{pr} \qquad (29)$$

If the net charges are small or equal to zero, $n_p \sim q_p$ and:

$$L\uparrow_{pp} = L_{pp} + \frac{1}{2} (q\downarrow_p - q\uparrow_p) C_{pp} = L_{pp} - \frac{1}{2} \varrho_p C_{pp} \qquad (30)$$

L_{pp} being the diagonal matrix element of the RHF model (17) corresponding to the neutral atom P.

$$\varrho_p = q\uparrow_p - q\downarrow_p \qquad (31)$$

is the spin density.

Likewise, we have:

$$L\downarrow_{pp} = L_{pp} + \frac{1}{2} (q\uparrow_p - q\downarrow_p) C_{pp} = L_{pp} + \frac{1}{2} \varrho_p C_{pp} \qquad (32)$$

For the off-diagonal elements, we obtain:

$$\begin{cases} L\uparrow_{pq} = I_{pq} - l\uparrow_{pq} C_{pq} = L_{pq} + \frac{1}{2} (l\downarrow_{pq} - l\uparrow_{pq}) C_{pq} \\ L\downarrow_{pq} = L_{pq} + \frac{1}{2} (l\uparrow_{pq} - l\downarrow_{pq}) C_{pq} \end{cases} \qquad (33)$$

We should note (cf 14) that:

$$l_{pq} = l\uparrow_{pq} + l\downarrow_{pq} \qquad (34)$$

In short, we shall write:

$$\begin{cases} \alpha\uparrow_p = \alpha_p - \frac{1}{2} \varrho_p C_{pp} \\ \alpha\downarrow_p = \alpha_p + \frac{1}{2} \varrho_p C\alpha_p \end{cases} \qquad \begin{cases} \beta\uparrow_{pq} = \beta_{pq} + \frac{1}{2} (l\downarrow_{pq} - l\uparrow_{pq}) C_{pq} \\ \beta\downarrow_{pq} = \beta_{pq} - \frac{1}{2} (l\downarrow_{pq} - l\uparrow_{pq}) C_{pq} \end{cases} \qquad (35)$$

where the α_p and β_{pq} are the RHF-Hückel parameters, corresponding to the neutral atoms. Consequently, this formalism appears as an iterative Hückel procedure. Starting from the RHF molecular orbitals, we must built up the secular equations corresponding to both $\uparrow$ and $\downarrow$ families. The molecular orbitals obtained allow us to obtain improved secular equations. And so on, up to the convergence.

The electron energy is:

$$E_e = \frac{1}{2} \sum_i \uparrow (I\uparrow_i + e\uparrow_i) + \frac{1}{2} \sum_j \downarrow (I\downarrow_j + e\downarrow_j) \qquad (36)$$

Taking into account the above equations, the UHF energy can be written:

$$E_{UHF} = \sum_i \uparrow e\uparrow_i + \sum_j \downarrow e\downarrow_j - \sum_p q\uparrow_p q\downarrow_p C_{pp} + \sum_{(pq)} [(l\uparrow_{pq})^2 + (l\downarrow_{pq})^2] C_{pq} - \sum_{(pq)} q_p q_q C_{pq} \qquad (37)$$

Moreover, we have for the $\sum\uparrow e\downarrow_i$ summation the relation:

$$\Sigma\uparrow e\uparrow_i = \Sigma L\uparrow_{pp} q\uparrow_p + 2 \Sigma L\uparrow_{pq} l\uparrow_{pq} \tag{38}$$

This general relation gives:

$$\Sigma\uparrow e\uparrow_i = \Sigma [L_{pp} + \frac{1}{2}(q\downarrow_p - q\uparrow_p) C_{pp}] q\uparrow_p + 2 \Sigma [L_{pq} + \frac{1}{2}$$

$$(l\downarrow_{pq} - l\uparrow_{pq}) C_{pq}] l\uparrow_{pq} = \Sigma L_{pp} q\uparrow_p + 2 \Sigma l\uparrow_{pq} + \frac{1}{2}$$

$$\Sigma [q\uparrow_p q\downarrow_p - (q\downarrow_p)^2] C_{pp} + \Sigma [l\uparrow_{pq} l\downarrow_{pq} - (l\uparrow_{pq})^2] C_{pq} \tag{39}$$

and the analog expression for $\Sigma\downarrow e\downarrow$.

The UHF electron energy (37) becomes:

$$E_{UHF} = \Sigma q_p L_{pp} + 2 \Sigma l_{pq} L_{pq} - \frac{1}{2} \Sigma q_p^2 C_{pp} + \frac{1}{2} \Sigma l_{pq}^2 C_{pq} - \Sigma q_p q_q C_{pq} -$$

$$- \frac{1}{4} \Sigma (q\uparrow_p - q\downarrow_p)^2 C_{pp} - \frac{1}{2} \Sigma (l\uparrow_{pq} - l\downarrow_{pq})^2 C_{pq} \tag{40}$$

This expression generalizes the RHF expression (21), that is valid even if all the φ space-functions are not used twice, under the condition that the factor 2 in the (12) and (14) relations is replaced by the number n_i (1 or 2) of molecular orbitals corresponding to the orbital energy e_i.

In so far as we can consider that the UHF procedure results from a perturbation in the RHF procedure, the charges (12) and the bond orders (14) are not changed. From equations (21) and (40), we conclude that the corresponding energy variation is:

$$E_{RHF} - E_{UHF} \sim \frac{1}{4} \Sigma \varrho^2_p C_{pp} + \frac{1}{2} \Sigma (l\uparrow_{pq} - l\downarrow_{pq})^2 C_{pq} \tag{41}$$

(the spin densities and the bond orders correspond to the RHF model). This difference is positive. The breakdown of the spin restriction produces a decrease of the energy, as we had to wait.

Remark on the $\hat{S}^2$ Operator

It is well known that in the UHF model the single determinant function is not the eigenfunction of the $\hat{S}^2$ operator. This operator can be explicated as a function of the monoelectronic spin operators:

$$\hat{S}^2 = \Sigma \hat{S}^2(\mu) + 2 \Sigma \hat{S}(\mu) \cdot \hat{S}(\nu) \tag{42}$$

If we take N as the total number of used molecular orbitals, the average value of $\hat{S}^2$ is:

$$<\hat{S}^2> = \frac{3N}{4} + \Sigma (2s_i s_j - S_{ij}^2) \tag{43}$$

where i and j are the used space-molecular orbitals, s_i and s_j the corresponding eigenvalues of the operator $\hat{S}_z$, and S_{ij} the overlap integral $\langle \varphi_i \varphi_j \rangle$. If we take $N\uparrow$ and $N\downarrow$ as the respective numbers of the spin-orbitals $\uparrow$ and $\downarrow$, we obtain:

$$<\hat{S}^2> = \frac{N}{2} + \frac{1}{4}(N\uparrow - N\downarrow)^2 - \Sigma S_{ij}^2 \tag{44}$$

In the RHF model, where the space functions are twice or singly utilized, this average value coincides with the eigenvalue of S^2:

$$S(S+1) = \frac{\nu(\nu+2)}{4} \tag{45}$$

with $\nu = N\uparrow - N\downarrow$ (on the assumption that $N\uparrow > N\downarrow$) $\qquad$ (46)

In the UHF model, we have:

$$<\hat{S}^2> - S(S+1) = N\downarrow - \sum_{(ij)} S_{ij}^2 \tag{47}$$

The UHF wave function is not an eigenvalue of the S^2 operator; the value of the difference (47) can be used as a criterion for testing the validity of the model. Since the $\hat{S}^2$ and $\hat{H}$ (2) operators commute, the smaller this difference, the more valid the single determinant approximation. Under this condition, it appears that it is not necessary to use the spin projection operators[9] to improve the description of the system. Moreover, this laborious operation is carried out only exceptionally. In particular, the standard UHF programmes used by chemists do not allow this operation.

SOME APPLICATIONS TO RADICALS AND METALLIC CLUSTERS

The Allyl Radical (reduced to the π-system)

We start from the RHF-Hückel functions[10]:

$$\begin{cases} \varphi\uparrow_1 = \varphi\downarrow_1 = \dfrac{1}{2}\,\chi_1 + \dfrac{1}{\sqrt{2}}\,\chi_2 + \dfrac{1}{2}\,\chi_3 \\[2mm] \varphi\uparrow_2 = \dfrac{1}{\sqrt{2}}\,(\chi_1 - \chi_3) \end{cases}$$

The corresponding charges and bond orders are:

$$q\uparrow_1 = q\uparrow_3 = 3/4; \quad q\downarrow_1 = q\downarrow_3 = 1/4; \quad q\uparrow_2 = q\downarrow_2 = 1/2$$

$$(\varrho_1 = \varrho_3 = 0.5; \quad \varrho_2 = 0)$$

$$l\uparrow_{12} = l\uparrow_{23} = l\downarrow_{12} = l\downarrow_{23} = \sqrt{2}/4$$

According to the relations (35), the new parameters are:

$$\begin{cases} \alpha\uparrow_1 = \alpha\uparrow_3 = \alpha - \eta \\ \alpha\uparrow_2 = \alpha \end{cases} \qquad \begin{cases} \alpha\downarrow_1 = \alpha\downarrow_3 = \alpha + \eta \\ \alpha\downarrow_2 = \alpha \end{cases} \qquad \text{(with } \eta = \frac{1}{4}\,C_{11})$$

$$\beta\uparrow_{12} = \beta\downarrow_{12} = \beta\uparrow_{23} = \beta\downarrow_{23} = \beta.$$

In the numerical calculations, we shall use the following values[11]:

$$C_{11} = 9.8 \text{ eV}, \quad \beta = 0.8\,\beta_0 \text{ with } \beta_0 \text{ (ethylen)} = -6.5 \text{ eV}.$$

Only two repetitions are necessary to obtain the convergence. The orbital energies values are:

Family $\uparrow$: $\alpha + 1.65\ \beta$; $\quad \alpha + 0.55\ \beta$; $\quad \alpha - 1.26\ \beta$

Family $\downarrow$: $\alpha + 1.26\ \beta$; $\quad \alpha - 0.55\ \beta$; $\quad \alpha - 1.65\ \beta$.

Consequently, we obtain the same utilization of the orbitals as the one which we have postulated at the start: $\varphi\uparrow_1 \varphi\downarrow_1 \varphi\uparrow_2$. The π-electron charges are practically equal to 1:

$$q_1 = q_3 = 1.01 \quad \text{and} \quad q_2 = 0.98.$$

The spin densities:

$$\varrho_1 = \varrho_3 = 0.57 \quad \text{and} \quad \varrho_2 = -0.13.$$

The bond orders $l\uparrow$ and $l\downarrow$ remain practically equal. The average value of S^2 is 0.76. (The eigenvalue corresponding to a doublet state is 0.75). According to (41), the energy decrease is equal to 0.23 $C_{11} \sim 2.3$ eV.

An open-shell SCF calculation[12] gave $\varrho_1 = \varrho_3 \sim 0.8$ and $\varrho_2 \sim -0.6$. These values were obtained from non-reduced electron integrals ($C_{11} = 16.9$ eV for example). Necessarily, the electron densities are greater than in this present work.

Square Molecules. Correlation with the Hund Rule

First, let us consider a symmetrical square system (cyclobutadien reduced to their π-electrons, Li$_4$ cluster). In the RHF model, according to the Hund rule, the utilized molecular orbitals are[10]:

$$\begin{cases} \varphi\uparrow_1 = \varphi\downarrow_1 = \dfrac{1}{2}\, (\chi_1 + \chi_2 + \chi_3 + \chi_4) \\[2mm] \varphi\uparrow_2 = \dfrac{1}{\sqrt{2}}\, (\chi_1 - \chi_3) \\[2mm] \varphi\uparrow_3 = \dfrac{1}{\sqrt{2}}\, (\chi_2 - \chi_4) \end{cases}$$

The orbital energies in the UHF model are:

Family $\uparrow$: $\alpha + 2\beta - \eta$; $\quad \alpha - \eta$ (twice); $\quad \alpha - 2\beta - \eta$

Family $\downarrow$: $\alpha + 2\beta + \eta$; $\quad \alpha + \eta$ (twice); $\quad \alpha - 2\beta + \eta$

with $\eta = C_{11}/4$.

The expressions of the molecular orbitals are unchanged. We obtain the same structure $\varphi\uparrow_1 \varphi\downarrow_1 \varphi\uparrow_2 \varphi\uparrow_3$ as in the RHF model, but without it being necessary to use the Hund rule. The spin density is equal to 1/2 for all the atoms. The decrease in energy is equal to η, i. e. ~ 2.5 eV in the cyclobutadien and ~ 1.2 eV in Li$_4$. The average value of S^2 is equal to 2; that is the eigenvalue for a triplet state.

The situation becomes more complex in the $\begin{matrix} \text{Li—Na} \\ | \quad | \\ \text{Na—Li} \end{matrix}$ cluster. If we take

$a_1 = a + \dfrac{\delta}{2}\beta$ and $a_2 = a - \dfrac{\delta}{2}\beta$ as the diagonal elements corresponding respectively to Li and Na atoms $a_2 > a_1$ because Li electronegativity (0.9) is greater than that of the Na atom (0.8). ($\beta < 0$, $\delta > 0$).

According to the reference[13]:

$$a_1 \sim -3.0 \text{ eV} \qquad a_2 \sim -2.8 \text{ eV}$$

$$\beta \sim -2.0 \text{ eV} \qquad (\delta \sim 0.1)$$

In the usual Hückel model, we obtain the orbital energies:

$$e_1 = \alpha + 2\beta\sqrt{1 + \delta^2/16} \sim \alpha + 2\beta; \quad e_2 = \frac{\delta}{2}\alpha + \frac{\delta}{2}\beta; \quad e_3 = \alpha - \frac{\delta}{2}\beta; \ldots$$

which lead to a ground state for the diamagnetic RHF structure:

$$\varphi\uparrow_1 \varphi\downarrow_1 \varphi\uparrow_2 \varphi\downarrow_2$$
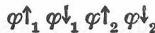
In this structure, a large asymmetry appears between the Li and Na atoms·

$$q_{Li} \sim \frac{3}{2} + \frac{\delta}{4} \text{ and } q_{Na} \sim \frac{1}{2} - \frac{\delta}{4}$$

This asymmetry is physically unacceptable because the difference between the Li and Na electronegativities is very small. Moreover, at the limit, if δ tends to zero, these charge values do not converge on the values corresponding to the symmetrical situation, which we have obtained above for Li_4.

In return, the results become acceptable in a structure which would generalize the Hund rule, extended to levels considered as sufficiently neighbouring: $\varphi\uparrow_1 \varphi\downarrow_1 \varphi\uparrow_2 \varphi\uparrow_3$. The corresponding electron charges become:

$$q_{Li} \sim 1 + \frac{\delta}{4} \qquad \text{and } q_{Na} \sim 1 - \frac{\delta}{4}$$

On this assumption, the highest level $\uparrow$ $(e\uparrow_3 = \alpha_2 - \frac{1}{2}C_{22} \sim -4.0$ eV) is located over the lowest level $\downarrow$ $(e\downarrow_2 = \alpha_1 + \frac{1}{4}C_{11} \sim -1.8$ ev). This relative disposition leads quite to the postulated structure.

In other words, the quasidegeneracy obtained in the RHF model for the levels 2 and 3, would permit the application of the Hund rule. Consequently, like Li_4, Li_2Na_2 would be paramagnetic.

This example shows clearly that the Hund rule (extended if necessary) is only a palliative which is indispensable in the RHF model, but to which it is not necessary to appeal in the more general UHF model.

One point remains a mystery. Owing to the Hund rule, at least in atoms, the system is in the state which corresponds to the greatest spin-multiplicity. That does not signify, as it is often said, that the electron spins are parallel. For example, in the triplet state, we have not only the two $\uparrow\uparrow$ and $\downarrow\downarrow$ components, but also the $(\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2}$ component corresponding to the eigenvalue zero of $\hat{S}_z$. The UHF model does not deal with the states corresponding to non-maximum spin components. It knows only the two states which correspond to a maximum magnetization. The question is whether the other states exist in reality. We shall return subsequently to this problem later.

The K_{15} BCC Cluster

Let us consider the K_{15} cluster representing the bcc structure, built up upon a potassium atom *1*, surrounded by their eight nearest-neighbours (*2* to *9*)

and their six second neighbours (10 to 15). We shall use the following parameters obtained from a systematic study of the alkali metals[11]:

$$\begin{cases} C_{11} = 3.8 \text{ eV}; & C_{23} = 1.6 \text{ eV} & (R_{12} = 4.62 \text{ Å}) \\ \beta_{12} = \beta; & \beta_{23} = 0.42 \ \beta & \text{with } \beta = -1.0 \text{ eV} \end{cases}$$

Starting from the RHF molecular orbitals, after two iterations, we obtain the following orbital energies:

Family $\uparrow$: $\alpha + 5.237 \ \beta$; $\alpha + 2.340 \ \beta$ (threefold); $\alpha - 0.027 \ \beta$;

$\alpha - 0.044 \ \beta$ (twofold); $\alpha - 0.118 \ \beta$ (threefold); ...

Family $\downarrow$: $\alpha + 5.058 \ \beta$; $\alpha + 2.112 \ \beta$ (threefold); $\alpha + 0.044 \ \beta$ (twofold);

$\alpha + 0.027 \ \beta$; $\alpha - 0.722 \ \beta$ (threefold); ...

Consequently, 8 $\uparrow$ levels and 7 $\downarrow$ levels are utilized by the 15 electrons. The electron charges and the spin densities are:

$q_1 = 1.55$;　$q_2 = \ldots = q_9 = 0.68$;　$q_{10} = \ldots q_{15} = 1.33$

$\varrho_1 = -0.01$;　$\varrho_2 = \ldots = \varrho_9 = 0.15$;　$\varrho_{10} = \ldots \varrho_{15} = -0.03$

The cluster is weakly paramagnetic. The average value of S^2 is 0.75 as in a doublet state.

In the RHF model: $\varrho_1 = \varrho_{10} = \ldots = \varrho_{15} = 0$

and $\varrho_2 = \ldots = \varrho_9 = 0.125$.

Tetrahedral Clusters

At first, we consider an alkali M_4 cluster (Li_4 for example). The RHF molecular orbitals are:

$$\begin{cases} \varphi\uparrow_1 = \varphi\downarrow_1 = \dfrac{1}{2} \ (\chi_1 + \chi_2 + \chi_3 + \chi_4) \\[2mm] \varphi\uparrow_2 = \varphi\downarrow_2 = \dfrac{1}{2} \ (\chi_1 + \chi_2 - \chi_3 - \chi_4) \\[2mm] \varphi\uparrow_3 = \varphi\downarrow_3 = \dfrac{1}{\sqrt 2} \ (\chi_1 - \chi_3) \\[2mm] \varphi\uparrow_4 = \varphi\downarrow_4 = \dfrac{1}{\sqrt 2} \ (\chi_2 - \chi_4) \end{cases}$$

According to the Hund rule, in order to respect the equivalence of the four corners, we must use in the Hückel method the molecular structure: $\varphi\uparrow_1 \ \varphi\downarrow_1 \ (\varphi\uparrow_2)^{2/3} \ (\varphi\uparrow_3)^{2/3} \ (\varphi\uparrow_4)^{2/3}$, in which the net charges are equal to zero and the bond orders equal to one another. Such a scheme corresponds to the linear combination

$$| \varphi\uparrow_1 \ \varphi\downarrow_1 \ \varphi\uparrow_2 \ \varphi\uparrow_3 | + | \varphi\uparrow_1 \ \varphi\downarrow_1 \ \varphi\uparrow_3 \ \varphi\uparrow_4 | + | \varphi\uparrow_1 \ \varphi\downarrow_1 \ \varphi\uparrow_4 \ \varphi\uparrow_2 |$$

In the UHF model, the orbital energies are the following:

Family ↑ : $\alpha + 3\beta - \eta$; $\alpha - \eta$ (threefold)

Family ↑ : $\alpha + 3\beta - \eta$; $\alpha - \eta$ (threefold) $\eta = C_{11}/4$).

The situation is the same as in the RHF model. We have three molecular orbitals ↑, threefold degenerate, for two electrons. The spin density is equal to 1/2 for each atom. The electron charges are equal to 1. The energy decrease is equal to ~ 1.2 eV. Here, again the average value of S^2 (0.75) coincides with the eigenvalue corresponding to a quartet state.

Now assume that each atom M carries three equivalent atomic orbitals--p-like for example — pointing in the directions of the neighbouring corners of the cube in which the tetrahedron can be drawn:
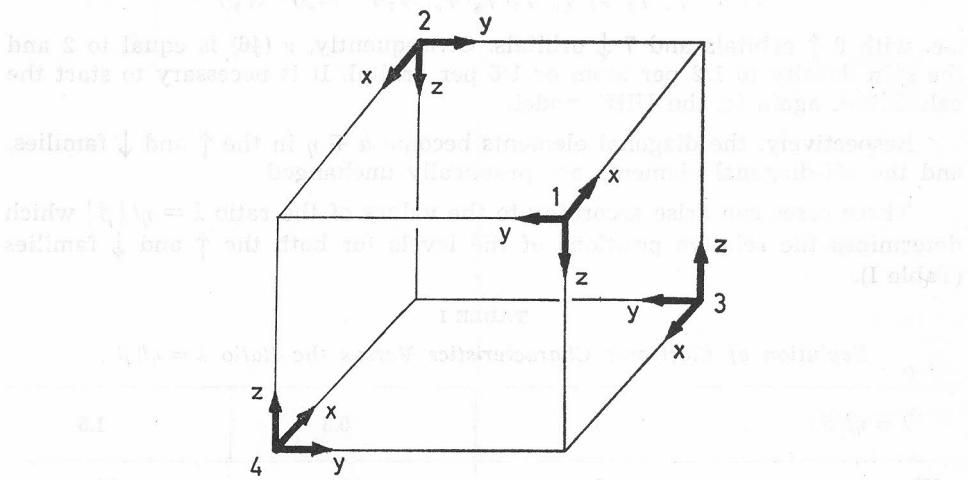
We shall call these orbitals p_x, p_y, p_z, in accordance with the direction of their axes.

We have three kinds of β term:

$$(p_{z_1}, p_{z_2}) = \beta; \quad (p_{x_1}, p_{x_2}) = \beta' \quad \text{and} \quad (p_{x_1}, p_{y_2}) = \beta''$$

If we assume that the β's are proportional to the corresponding orbital overlap integrals, we can write:

$$\beta' = (k - 1)\,\beta/2 \quad \text{and} \quad \beta'' = (k + 1)\,\beta/2$$

k being the ratio of the overlap integral corresponding to the two p-orbitals carried by the atoms 1 and 2, pointing at one another along the nuclei line ($\sigma\sigma$-like), and the overlap integral corresponding to the parallel orbitals p_{z_1} and p_{z_2} ($\pi\pi$-like). The coefficient k is greater than the unity. In the calculation we have used $k = 2$. Consequently:

$$\beta' = \beta/2 \quad \text{and} \quad \beta'' = 3\beta/2.$$

In the RHF model, we obtain the twelve orbital energies:

$\alpha + 5\,\beta$; $\alpha + 2.386\,\beta$ (threefold); $\alpha + 0.5\,\beta$ (twofold);

$\alpha - 1.386\,\beta$ (threefold); $\alpha - 0.5\,\beta$ (threefold).

If each atom brings *two* electrons (= 8 electrons for the whole cluster), the molecular structure corresponds to $(\varphi_1^2\,\varphi_2^2\,\varphi_3^2\,\varphi_4^2)$. The cluster is diamagnetic. Likewise, if each atom brings *three* electrons (= 12 electrons for the whole cluster) the structure corresponds to: $(\varphi_1^2\,\varphi_2^2\,\varphi_3^2\,\varphi_4^2\,\varphi_5^2\,\varphi_6^2)$. In neither case it is necessary to use the UHF model.

The situation becomes completely different if each atom brings *four* electrons (16 electrons for the system). According to the Hund rule, the symmetrical structure corresponds to:

$$\varphi_1^2\,\varphi_2^2\,\varphi_3^2\,\varphi_4^2\,\varphi_5^2\,\varphi_6^2\,\varphi_7{\uparrow}\,\varphi_8{\uparrow}\,\varphi_9{\uparrow}\,(\varphi_7{\downarrow})^{1/3}\,(\varphi_8{\downarrow})^{1/3}\,(\varphi_9{\downarrow})^{1/3}$$

i. e. with 9 ↑ orbitals and 7 ↓ orbitals. Consequently, ν (46) is equal to 2 and the spin density to 1/2 per atom or 1/6 per orbital. It is necessary to start the calculation again in the UHF model.

Respectively, the diagonal elements become $\alpha \mp \eta$ in the ↑ and ↓ families, and the off-diagonal elements are practically unchanged.

Three cases can arise according to the values of the ratio $\lambda = \eta/|\beta|$ which determines the relative positions of the levels for both the ↑ and ↓ families (Table I).

TABLE I

Evolution of Electronic Characteristics Versus the Ratio $\lambda = \eta/|\beta|$.

$\lambda = \eta/|\beta|$	0	0.3	1.5
N↑	9	10	12
N↓	7	6	4
$\nu = $ N↑ $-$ N↓	2	4	8
ϱ (per orbital)	1/6	1/3	2/3
μ_{at} (in μ_B)	1.1	1.7	2.8
η	$C_{11}/12$	$C_{11}/6$	$C_{11}/3$
$E_{RHF} - E_{UHF}$	$C_{11}/12$	$C_{11}/3$	$4C_{11}/3$

In the three ranges $(0 < \lambda < 0.3)$, $(0.3 < \lambda < 1.5)$ and $(1.5 < \lambda)$, the values of the ratio $\gamma = C_{11}/|\beta|$ are respectively:

$$0 < \gamma < 3.6;\quad 1.8 < \gamma < 9\quad \text{and}\quad 4.5 < \gamma.$$

Taking into account the energy decreases, the ground states correspond respectively to $\nu = 2$ if $0 < \gamma < 1.8$, to $\nu = 4$ if $1.8 < \gamma < 4.5$, and to $\nu = 8$ if $4.5 < \gamma$.

In other words, when the ratio $C_{11}/|\beta|$ is small, we obtain the same spin density as in the RHF model ($\nu = 2$), and when this ratio increases, we obtain successively $\nu = 4$ and $\nu = 8$. The paramagnetism of the cluster is strongly increased. The spin density can become equal to that found in bulk ferromagnetic metals (about 2.2 μ_B per atom in iron for example).

If each atom brings *five* electrons (20 electrons for the whole cluster), according to the Hund rule, the RHF structure corresponds to:

$$\varphi_1^2 \, \varphi_2^2 \, \varphi_3^2 \, \varphi_4^2 \, \varphi_5^2 \, \varphi_6^2 \, \varphi_7^2 \, \varphi_8^2 \, \varphi_9^2 \, (\varphi_{10}\uparrow)^{2/3} \, (\varphi_{11}\uparrow)^{2/3} \, (\varphi\uparrow_{12})^{2/3}.$$

We have 11 orbitals $\uparrow$ and 9 orbitals $\downarrow$ ($\nu = 2$, $\varrho = 1/6$).

By means of calculations similar to those made in the previous case, one sees that $\nu = 2$ ($\varrho = 1/6$) when $\eta/|\beta| < 0.6$, and $\nu = 4$ ($\varrho = 1/3$) when $\eta/|\beta| > 0.6$. The decreases in energy are respectively equal to $C_{11}/12$ and $C_{11}/3$. When the ratio $C_{11}/|\beta|$ increases, the paramagnetism increases, but in a proportion not as strong as in the previous case.

Finally, if each atom brings *six* electrons, the cluster is diamagnetic.

The results obtained in the case of the tetrahedron show clearly that the breakdown of the spin restriction does not produce only a decrease in energy. Sometimes, it can provoke a modification of the respective number of $\uparrow$ and $\downarrow$ molecular orbitals, larger than that the classical Hund rule would require. Moreover, it is interesting to remark that the values of the paramagnetism which results from this modification can be equal, even in small size clusters, to those in ferromagnetic metals. Thus the properties of the Weiss domains should be explained. According to the classical theory, these domains have the maximum magnetization; the effect of the exterior magnetic field is not to create this magnetization, but only to allow its observation[14]. Perhaps that is the answer to the question which we posed at the end of the previous section. In a finite size cluster, only the states given by the UHF model, for which the $\hat{S}_z$ — components are maximum, should exist.

However, the schematic example of the tetrahedral cluster can help us to understand the evolution of the magnetic properties in the transition elements. In this group, $|\beta|$ is in the range 1 to 2 eV, and the integral C_{11} varies from 6 to 8 eV, from scandium to nickel. Consequently, the ratio γ is located in the neighbourhood of a value which is approximatively equal to the critical value 4.5 obtained in a system having a weaker number of orbitals per atom. The first transition elements are weakly paramagnetic. Those located in the middle of the group have a strong magnetization, which decreases in the last elements. By means of $X\alpha$-calculations the V_{15} cluster is obtained as weakly paramagnetic, the Fe_{15} whole cluster as strongly paramagnetic[3]. The average value of the magnetic moment is about 2.6 μ_B per atom. This value is close to the one observed in bulk iron (2.2 μ_B). Analogous results are obtained for the tetrahedral clusters[15].

Antiferro- and Ferrimagnetic Clusters

The above example shows that the method is able to explain the ferromagnetic properties. This method allows also to study antiferro — or ferrimagnetic systems. As an example, we have choosen a square molecule
$$\begin{matrix} A & — & B \\ | & & | \\ B & — & A \end{matrix}$$
in

which the A carry atoms only an s-orbital and the B atoms two p-orbitals pointing respectively towards the A atoms. We shall suppose that each A atom brings *two* electrons, and each B atom, n electrons. We shall use the following parameters (in eV):

$$\alpha_p = \alpha_s + 2; \quad \beta_{sp} = -1; \quad C_{ss} = 8; \quad C_{pp} = 4.$$

(the other parameters β are assumed equal to zero).

In the RHF model, we have three pairs of degenerated levels. Consequently, if the total number of electrons is equal to four (n = 0), we obtain all the spin densities equal to zero. The molecular energies corresponding to the utilized levels are:

$$e_1{\uparrow} = e_1{\downarrow} = e_2{\uparrow} = e_2{\downarrow} = -0.732.$$

In the UHF model, starting from slightly different $L^{\uparrow}$ and $L^{\downarrow}$ values, the differences between the diagonal elements increase, and finally converge to the structure corresponding to the orbital energies:

$$e_1{\uparrow} = e_2{\uparrow} = -2.722 \quad \text{and} \quad e_1{\downarrow} = e_2{\downarrow} = 0.400$$

The obtained total energy is about 1.8 eV lower than the energy of the initial RHF structure. This situation arises from the instability of the diagonal elements I_{pp}. The corresponding spin densities are different from zero:

$$\varrho_A = -\varrho_B = 0.6$$

These values correspond typically to an antiferromagnetism (cf. NiO). The breakdown of the spin restriction is necessary to obtain this situation.

If each atom B brings n = 1 electron, we have 4 molecular orbitals ↑ and 2 molecular orbitals ↓. The spin densities are respectively $\varrho_A = -0.5$ and $\varrho_B = 1.5$. These values correspond to a ferrimagnetism (cf. spinels).

CONCLUSION AND OUTLOOKS

The above applications show clearly the possibilities of the Hückel method extended to the UHF model. Still, owing to the simplicity of the method, its principal interest is to allow the study of clusters having a great number of atoms (many hundreds), which are, at the present time, unapproachable by means of the other methods.

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SAŽETAK

Neograničena Hartree-Fockova samousklađena Hückelova metoda. Primjena na magnetska svojstva radikala i metalnih grozdova

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Hückelova metoda, koja se može smatrati samousklađenom metodom u Löwdinovoj bazi, proširena je u UHF model. Opisane su neke primjene te metode na -radikala i metalne grozdove. Diskutira se korelacija s Hundovim pravilom. Pokazano je podrijetlo jake magnetizacije elemenata smještenih u sredinu periode prijelaznih elemenata. Dani su primjeri antiferimagnetičnih i ferimagnetičnih grozdova.

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