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Commentationes

General Properties of the Hartree-Fock Problem Demonstrated on the Frontier Orbital Model

I. Relation among Various Types of Extrema*

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The general Hartree-Fock energy in the frontier orbital model in the terms of independent variables is given. The existence conditions for extrema of this expression are derived and their relation with various types of solutions of the HF problem as RHF, UHF and complex wavefunctions is shown. The connection between overall properties of the energy surface and the local properties i.e. the stability and instability conditions of various kinds is demonstrated. The conditions for the occurrence of "strange" HF solutions are expressed in terms of quantities characterizing the correlation effects. This shows explicitly that the lack of respecting the electronic correlation is the reason for the occurrence of the "strange" HF solutions for the molecular configurations which exhibit a certain amount of diradical character.

Key words: Hartree-Fock-problem – Frontier molecular orbital model

1. Introduction

As it is well known, during the chemical reactions and molecular rearrangements the nonequilibrium molecular geometrical configurations can exhibit a certain amount of spin decoupling. In the concerted reactions due to the delocalization of the electrons involved in breaking and creating bonds, the overall spin decoupling can be fairly small. Therefore, in such cases, the one-electron description of the reaction path can be successfully used (Woodward-Hoffmann rules). If the reaction proceeds through the intermediates of diradical or diradical-like character, the appropriate description of spin decoupling is crucial. It is obvious that besides the two above mentioned extreme situations the in-between cases can occur i.e. a certain amount of spin decoupling exists in spite of the electron delocalization. Therefore, the applicability of the one-electron approach for description of the reaction path must be critically and carefully examined. In fact, various physically unacceptable solutions of the Hartree-Fock problem (which is in general of complicated mathematical nature [1–5]) arise just for the molecular geometries sufficiently far from the equilibrium ones.

It is possible to obtain symmetry nonadapted restricted HF (RHF) solutions for symmetrical molecules [6, 7, 14, 15], unrestricted HF (UHF) for closed shell

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molecules [6–15], complex HF solutions [16–20] and additional RHF symmetry adapted solutions [21, 22].

The customary iterative procedure [23] used for solving the HF problem exhibits further strange ("pathological") properties when the iterative process does not end with the Slater determinant, which can be considered as a solution of the HF problem [24, 25].

The occurrence of the strange HF solutions for certain molecular geometries of similar character (mainly nonequilibrium ones) indicates the existence of the common physical background, probably in an improper description of the electronic configurations by the one-electron approximation. It has been shown [10, 24] that even small deviation from equilibrium geometries for polyenic chains give rise to the strange HF solutions which can be taken as indication of the presence of diradical character[1].

The analysis of the HF problem and the connection among the HF solutions of the various kinds is important from two points of view. First, for determining the limits of the applicability of one electron approximation, which is still the most widely used approach for describing the reaction path. Secondly, the failure of the one-electron approach to give the physically acceptable solutions can be taken as indication of diradical character for molecules for which the presence of diradical properties cannot be seen at the first glance.

The purpose of the analysis presented in this work is to find the common reason and mutual relations of the described strange properties of the HF approach. The explicit analysis is carried out in this paper and the accompanying one on the two-electron system in the minimal basis set (two-orbital model).

The frontier orbital model of Fukui is of such nature (cf. [19, 20]) and can be used when the electronic structure of a polyatomic molecule is substantially determined by one occupied and one unoccupied, most frequently the highest occupied and the lowest unoccupied molecular orbitals in the framework of the one-electron approximation. The frontier orbital model is particularly suitable for studying the electronic configurations in the neighborhood of the molecular orbital crossing.

In the frontier orbital model the energy expectation value for the corresponding Slater determinant is a simple expression in the terms of independent variables which enter through the one electron density matrix (compare [27]). This general HF energy expression gives the natural connection among various kinds of HF solutions: symmetry adapted and symmetry nonadapted, restricted, unrestricted and complex solutions.

In general, the HF solutions are extremum points on the energy surface in the general space Y of the independent variables [21, 27] and the HF energy. The HF solutions are obtained under various constraints which define the corresponding subspaces of the general space Y (compare also [4]). Visualization of this complicated space structure is possible in the case of simple frontier orbital model. The possible generalization to the more complicated cases can be easily made, as well.

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[1] Between the submission of the original and revised version of this paper following articles appeared: Yamaguchi, K., Fueno, T., Fukutome, H.: Chem. Phys. Letters **22**, 461 (1973); Gregory, A. R.: J. Chem. Phys. **60**, 1680 (1974).

2. Fukui's Frontier Molecular Orbital Model

The frontier orbital model describing the polyatomic molecule has formal similarity with a minimal basis description of a diatomic molecule, the main difference being in the bigger flexibility of molecular integrals (cf. [20]).

Frontier orbitals $|\Psi_k^\lambda\rangle$ occupied by the electron with the spin $\lambda(\lambda=\alpha,\beta)$ in the configuration k and the corresponding virtual unoccupied frontier orbitals $|\Psi_{\bar{k}}^\lambda\rangle$ can be taken as linear combination of suitable one-electron orthonormal functions.

$$|\Psi_k^\lambda\rangle = C_{11}^\lambda\,|\varphi_1\rangle + C_{12}^\lambda\,|\varphi_2\rangle\,, \tag{1}$$

$$|\Psi_{\bar{k}}^\lambda\rangle = C_{21}^\lambda\,|\varphi_1\rangle + C_{22}^\lambda\,|\varphi_2\rangle\,. \tag{2}$$

The one-electron functions $|\varphi_1\rangle$ and $|\varphi_2\rangle$ can be equivalent orbitals for symmetrical molecules or other functions. We assume in Eqs. (1) and (2) that the functions $|\varphi_j\rangle$ are not different for different spins, which does not have to be always exactly the case in the UHF approach. The spin labelled frontier MO's ($\lambda=\alpha,\beta$) make possible to carry out the analysis for RHF and UHF approach simultaneously. In the molecular orbital crossing the configurations k and $\bar{k}$ as defined above exchange the role.

Slater determinant formed by the frontier orbitals $|\Psi_k^\lambda\rangle$ for $\lambda=\alpha,\beta$ is [compare Eq. (A 1)]:

$$|D\rangle_k = \sqrt{2}\,\hat{A}\,|\Psi_k^\alpha, 1\rangle\,|\alpha, 1\rangle\,|\Psi_k^\beta, 2\rangle\,|\beta, 2\rangle\,. \tag{3}$$

One electron density matrix in the representation of $|\varphi_m\rangle$ [compare Eqs. (A 9) and (A 14)] takes the form:

$$\boldsymbol{P}^{T\lambda}(k) = \begin{pmatrix} |C_{k1}^\lambda|^2, & C_{k1}^{\lambda *}\,C_{k2}^\lambda \\ C_{k1}^\lambda\,C_{k2}^{\lambda *}, & |C_{k2}^\lambda|^2 \end{pmatrix}, \qquad \lambda=\alpha,\beta\,, \tag{4}$$

where

$$\boldsymbol{P}_{(k)}^{T\lambda} = \langle\mu|\hat{R}^c(k)|\nu\rangle + \langle\mu|\hat{R}^\lambda(k)|\nu\rangle\,. \tag{4a}$$

The first and second term in the Eq. (4a) are elements for the closed shell and open shell ($\lambda=\alpha$ or β) one-electron density matrix, respectively. The projector operators $\hat{R}^c(k)$ and $\hat{R}^\lambda(k)$ on the closed shell and open shell Fermi seas are given in the Appendix by Eqs. (A 2)–(A 4) [cf. also (A 9) and (A 14)].

From the idempotency relation

$$(\boldsymbol{P}^{T\lambda})^2 = \boldsymbol{P}^{T\lambda} \tag{5}$$

follows (compare also [24] and [27]):

$$P_{jj}^{T\lambda} = \tfrac{1}{2}\left(1-(-1)^{s(\lambda)+j}\sqrt{1-4p_\lambda^2}\right), \qquad j=1,2 \tag{6}$$

and

$$P_{12}^{T\lambda} = p_\lambda \exp(i\Phi_\lambda)\,, \qquad 0 \leqq \phi_\lambda \leqq 2\pi \tag{7}$$

where $s(\lambda)$ is an integer arising as a consequence of nonlinear idempotency relation valid for one electron density matrix [Eq. (5)].

The absolute value of the offdiagonal element of the one-electron density matrix is p_λ. If one-electron functions $|\varphi_m\rangle$ are atomic (or group) orbitals, then $P_{jj}^{T\alpha} + P_{jj}^{T\beta}$ and $P_{12}^{T\alpha} + P_{12}^{T\beta}$ are atomic (group) charges and bond orders, respectively. As only two electrons are taken in consideration, there are only two possibilities of electron distribution in Fermi seas which correspond to the restricted and unrestricted Hartree-Fock method. In the RHF α- and β-singly occupied Fermi seas are empty, i.e. $\hat{R}^\alpha = \hat{R}^\beta = 0$ [compare Eqs. (A3) and (A9)] and $\boldsymbol{P}^{T\alpha} = \boldsymbol{P}^{T\beta}$, i.e. $p_\alpha = p_\beta \equiv p$, $\Phi_\alpha = \Phi_\beta \equiv \Phi$ and $s(\alpha) = s(\beta) \equiv s$ or

$$P_{\mu\nu}^{T\alpha} = P_{\mu\nu}^{T\beta} \equiv P_{\mu\nu}\,. \tag{8}$$

In the UHF doubly occupied Fermi sea is empty, $\hat{R}^c = 0$ [compare Eq. (A2)] and $\boldsymbol{P}^{T\alpha} \neq \boldsymbol{P}^{T\beta}$, i.e. at least one of the following relations holds:

$$p_\alpha \neq p_\beta \quad \text{or} \quad \Phi_\alpha \neq \Phi_\beta \quad \text{or} \quad s(\alpha) \neq s(\beta)\,. \tag{9}$$

For RHF approach we name as "bond order" the quantity P_{12} defined by Eq. (8) which is $\frac{1}{2}$ of the customary used bond order $(P_{12}^{T\alpha} + P_{12}^{T\beta})$. Such definition of "bond order" is advantageous for simultaneous consideration of RHF and UHF approaches.

3. Energy Expectation Value for the Frontier Molecular Orbitals

The effective Hamiltonian of two electrons in the frontier orbitals is:

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + \hat{g}(1,2)\,. \tag{10}$$

When only the idempotency relation (5) is used [cf. Eqs. (6) and (7)], the energy expectation value $E = \langle D|H|D\rangle$ [Eq. (A6)] for the Slater determinant given by Eq. (3) takes the general form:

$$\begin{aligned} E' = E - (h_{11} + h_{22}) - \Gamma_{12} &= 2\beta'(p_\alpha \cos\Phi_\alpha + p_\beta \cos\Phi_\beta) \\ &+ \frac{\Delta}{2}\{1 + (-1)^{s(\alpha)+s(\beta)}[(1-4p_\alpha^2)(1-4p_\beta^2)]^{\frac{1}{2}}\} + 4K_{12}p_\alpha p_\beta \cos\Phi_\alpha \cos\Phi_\beta \\ &+ \frac{A}{2}[(-1)^{s(\alpha)}(1-4p_\alpha^2)^{\frac{1}{2}} + (-1)^{s(\beta)}(1-4p_\beta^2)^{\frac{1}{2}}] \\ &+ Z[(-1)^{s(\alpha)}(1-4p_\alpha^2)^{\frac{1}{2}}\,p_\beta \cos\Phi_\beta + (-1)^{s(\beta)}(1-4p_\beta^2)^{\frac{1}{2}}\,p_\alpha \cos\Phi_\alpha]\,. \end{aligned} \tag{11}$$

Matrix elements $h_{\mu\nu}$ are defined by Eq. (A7) and

$$\beta' = h_{12} + \tfrac{1}{2}[(11|12) + (22|21)]\,, \tag{12}$$

$$\Delta = \tfrac{1}{2}[(11|11) + (22|22)] - (11|22) = \tfrac{1}{2}(\Gamma_{11} + \Gamma_{22}) - \Gamma_{12}\,, \tag{13}$$

$$K_{12} = (12|12)\,, \tag{14}$$

$$A = h_{11} - h_{22} + \tfrac{1}{2}(\Gamma_{11} - \Gamma_{22})\,, \tag{15}$$

$$Z = (11|12) - (22|21)\,. \tag{16}$$

The general energy expression Eq. (11) will be used for studying the effect of introducing the specific constraints. The arbitrary linearly independent one-electron functions $|\varphi_1\rangle$ and $|\varphi_2\rangle$ [compare Eqs. (1) and (2)] forming a suitable two-dimensional basis for a frontier orbital model figure in all integrals from Eqs. (12)–(16) following the notation given by Eqs. (A7) and (A8). In the simplest case of two-dimensional one-electron density matrix Eq. (4) the energy E' Eq. (11) is a function of independent variables p_α, p_β, $\cos\Phi_\alpha$, $\cos\Phi_\beta$ and of the integers

$s(\alpha)$ and $s(\beta)$. For the n-dimensional case the energy in terms of independent variables, generalized Eulerian angles, is given in Ref. [27]. The energy expectation value E' [Eq. (11)] has extrema for the frontier MO's $|\Psi_k^\lambda\rangle$, which are eigen functions of the Hartree-Fock operator $\hat{F}^\lambda$ defined in general by Eq. (A 12).

It is possible to find the extrema of E' by carrying out derivatives with respect to the independent variables. This procedure is an alternative to the introduction of the Lagrange multipliers in the variational technique which leads to the pseudo eigen equations of the Hartree-Fock operator $\hat{F}^\lambda$.

4. Extrema of the Hartree-Fock Energy in the Representation of the Equivalent Orbitals

If the one-electron function $|\varphi_1\rangle$ from Eqs. (1) and (2) is transformed under the symmetry operation $\hat{T}(\hat{T}^2 = \hat{I})$ into $|\varphi_2\rangle$ as:

$$|\varphi_2\rangle = \hat{T}|\varphi_1\rangle \tag{17}$$

and vice versa, then these one-electron functions are equivalent orbitals and we name them $|\chi_1\rangle$ and $|\chi_2\rangle$. In this case $\Lambda = Z = 0$ in the energy expression given by Eq. (11). It is possible to show that the conditions for extrema of

$$E'\left(\frac{\partial E'}{\partial p_\lambda} = \frac{\partial E'}{\partial \Phi_\lambda} = 0,\, \lambda = \alpha, \beta\right)$$

are simultaneously satisfied if and only if $p_\alpha = p_\beta \equiv p$ and $\cos\Phi_\alpha = \cos\Phi_\beta \equiv \cos\Phi$. Therefore, we will consider the energy expression Eq. (11) in the basis of equivalent orbitals $|\chi_1\rangle$, $|\chi_2\rangle$ [Eq. (17)] under these limitations[2]:

$$E' = 4\beta' p\cos\Phi + \frac{\Delta}{2}[1 + (-1)^{s(\alpha)+s(\beta)}(1 - 4p^2)] + 4K_{12}p^2\cos^2\Phi\,. \tag{18}$$

Expressions β', Δ, and K_{12} defined by Eqs. (12)–(14) contain integrals in which now enter equivalent orbitals. The energy expression given by Eq. (18) can exhibit the following extrema which are simultaneously the only possible extrema of the more general energy expression [Eq. (11)].

a) For $\sin\Phi = 0$ and $\cos\Phi = \pm 1$, i.e. for the real "bond order" [Eq. (7)], E' exhibits extrema at the end of the interval of physically acceptable values for "bond order":

$$P_{12} = p\cos\Phi = \pm\tfrac{1}{2}\,. \tag{19}$$

These extrema are the only symmetry adapted HF solutions.

b) For $\sin\Phi = 0$ other extrema can occur if:

$$p = \frac{\beta'\cos\Phi}{(-1)^{s(\alpha)+s(\beta)}\Delta - 2K_{12}} \tag{20}$$

where $\cos\Phi = \pm 1$. Existence conditions for the extrema given by Eq. (20) are (compare [10]):

$$2\beta'\cos\Phi < (-1)^{s(\alpha)+s(\beta)}\Delta - 2K_{12}\,. \tag{21}$$

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[2] These conditions imply that for UHF approach $P_{12}^{T\alpha} = P_{12}^{T\beta}$, $P_{11}^{T\alpha} = P_{22}^{T\beta}$, and $P_{22}^{T\alpha} = P_{11}^{T\beta}$.

c) For $\sin\Phi \neq 0$, i.e. for the complex "bond order", the extremum is obtained if $p=\frac{1}{2}$ and $\cos\Phi = -\frac{\beta'}{K_{12}}$ i.e. if

$$P_{12} = -\frac{\beta'}{2K_{12}} \pm \frac{i}{2}\left(1-\left(\frac{\beta'}{K_{12}}\right)^2\right)^{\frac{1}{2}}. \tag{22}$$

The existence condition for this extremum is (compare [20]):

$$|\beta'| < K_{12}. \tag{23}$$

5. Stability and Instability of the Real Symmetry Adapted RHF Solution; UHF, Complex HF Solutions and Nonuniqueness of the Real RHF Problem

Let us consider the two-dimensional basis formed by the Vectors $|A\rangle$ and $|B\rangle$ defined as

$$|A\rangle = \frac{1}{\sqrt{2}}(|\chi_1\rangle + |\chi_2\rangle), \tag{24}$$

$$|B\rangle = \frac{1}{\sqrt{2}}(|\chi_1\rangle - |\chi_2\rangle), \tag{25}$$

where $|\chi_1\rangle$ and $|\chi_2\rangle$ are equivalent orbitals [cf. Eq. (17)]. Vectors $|A\rangle$ and $|B\rangle$ describe the energy extrema given by the real "bond order" $p=\frac{1}{2}$, $\cos\Phi = 1$ and $p=\frac{1}{2}$, $\cos\Phi = -1$, respectively [Eq. (19)]. The $|A\rangle$ and $|B\rangle$ are symmetry adapted real restricted HF solutions corresponding to the irreducible representations a and b of the symmetry group $(\hat{I}, \hat{T})$.

In order to determine if these symmetry adapted RHF solutions are minima or maxima, we investigate the energy expectation value

$$E_k^v = \langle D_k^v | \hat{H} | D_k^v \rangle. \tag{26}$$

A variational Slater determinant $|D_k^v\rangle$ is of the form given by Eq. (3) where

$$|\Psi_k^\lambda\rangle = |k\rangle + \delta_\lambda |\bar{k}\rangle, \quad \lambda = \alpha, \beta^3. \tag{27}$$

Compare also Refs. [19, 28]. A small variational parameter δ_λ can be generally a complex number. If $k=A$ then $\bar{k}=B$ and vice versa. If the variation remains in the framework of RHF then $\delta_\alpha = \delta_\beta \equiv \delta$. The variational functionals E_A^v and E_B^v will be used to investigate the behavior of these energy expectation values in the neighborhood of the Points $|A\rangle$ and $|B\rangle$ defined by $|\Psi_A^\alpha\rangle = |\Psi_A^\beta\rangle \equiv |A\rangle$ and $|\Psi_B^\alpha\rangle = |\Psi_B^\beta\rangle \equiv |B\rangle$. Expression for E_k^v Eq. (26) with integrals in terms of the Vectors $|A\rangle$ and $|B\rangle$ is obtained from Eq. (11) taking into account that the first order terms in variational parameters δ_λ vanish due to Brillouin theorem. For small δ_λ, $p_\lambda \cong |\delta_\lambda|$ and the terms higher then second order in δ_λ are neglected.

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[3] In the definition of variational molecular orbital Eq. (27) instead $|\bar{k}\rangle$ can be introduced any suitable Vector $|\varrho\rangle$ orthogonal to $|k\rangle$. Such generalized definition is convenient for one-electron orthonormal basis $|\mu\rangle$ of arbitrary dimension. For use of this basis compare Ref. [19]; Marshall, W.: Proc. Phys. Soc. (London) **78**, 113 (1961), and Musher, J. I.: Chem. Phys. Letters **7**, 397 (1970). All the results from the Section 5 are valid for such generalized basis as well.

Under these assumptions the variational energy E_k^v can be written:

$$\begin{aligned} E_k^v = 2h_{kk} + \Gamma_{kk} - (|\delta_\alpha|^2 + |\delta_\beta|^2)\,[h_{kk} - h_{\bar{k}\bar{k}} + \Gamma_{kk} - \Gamma_{k\bar{k}}] \\ + 4\,\mathrm{Re}(\delta_\alpha)\,\mathrm{Re}(\delta_\beta)\,K_{k\bar{k}} \end{aligned} \tag{28}$$

where

$$h_{kk} = \langle k|h(1)|k\rangle\,, \quad \Gamma_{kk} = (kk|kk)\,, \quad \Gamma_{k\bar{k}} = (kk|\bar{k}\bar{k})\,, \quad K_{k\bar{k}} = (k\bar{k}|k\bar{k}) \tag{28a}$$

with $k = A, B$ and $\bar{k} = B, A$ [compare also Eqs. (A 7) and (A 8)].

The energy expression given by Eq. (28) can be written in the form (compare also [19]):

$$\begin{aligned} E_k^v - E_k^{\mathrm{RHF}} = (|\delta_\alpha|^2 + |\delta_\beta|^2\,[{}^{1,3}E(k\rightarrow\bar{k}) \mp K_{k\bar{k}}] \\ + 4\,\mathrm{Re}(\delta_\alpha)\,\mathrm{Re}(\delta_\beta)\,K_{k\bar{k}}\,, \end{aligned} \tag{29}$$

where

$$E_k^{\mathrm{RHF}} = 2h_{kk} + \Gamma_{kk} \tag{30}$$

is restricted Hartree-Fock energy in the investigated extremum point k and

$${}^{1,3}E(k\rightarrow\bar{k}) = h_{\bar{k}\bar{k}} - h_{kk} - \Gamma_{kk} + \Gamma_{k\bar{k}} \pm K_{k\bar{k}}\,, \qquad k = A, B\,;\; \bar{k} = B, A) \tag{31}$$

are the singlet and triplet energies assigned to the singly excited configuration $k\rightarrow\bar{k}$ (compare [23]).

The neighborhood of the extremum Points $|A\rangle$ and $|B\rangle$ [Eqs. (24) and (25)] can be investigated in various directions using Eq. (29) with different assumptions upon variational parameters δ_α and δ_β.

a) If $\delta_\alpha = \delta_\beta = \mathrm{Re}\,(\delta)$ then variational parameters are under the constraints which characterize the real RHF problem [$|\Psi_k^\alpha\rangle = |\Psi_k^\beta\rangle$ from Eq. (27)]. The stability condition in the Point $|k\rangle$ i.e. the condition that the extremum in this point is a minimum follows from Eq. (29) in the form:

$${}^1E(k\rightarrow\bar{k}) + K_{k\bar{k}} > 0\,. \tag{32}$$

If in the definition of molecular orbitals Eq. (28a) the orbitals $|A\rangle$ and $|B\rangle$ are expressed in terms of equivalent orbitals $|\chi_1\rangle$ and $|\chi_2\rangle$ [Eqs. (24) and (25)] one obtains the stability condition given by Eq. (32) at the Point $|A\rangle$ (i.e. $p = \frac{1}{2}$, $\cos\Phi = 1$) in the representation of equivalent orbitals as:

$$-2\beta' + \Delta - 2K_{12} > 0\,. \tag{33}$$

For negative values of β' inequality (33) is satisfied for reasonable localization of $|\chi_1\rangle$ and $|\chi_2\rangle$ implying $\Delta > 2K_{12}$ (compare also [20]). In this section we will consider only the case of $\beta' < 0$. For $\beta' > 0$ the role of Points $|A\rangle$ and $|B\rangle$ is exchanged. The stability condition [Eq. (32)] at the Point $|B\rangle$ ($p = \frac{1}{2}$, $\cos\Phi = -1$) indicating the possibility of a maximum between $|A\rangle$ and $|B\rangle$ for real RHF is:

$$2\beta' + \Delta - 2K_{12} > 0\,. \tag{34}$$

This condition can be satisfied for large enough Δ or small enough $|\beta'|$ and it is equivalent to the existence condition Eq. (21) of the extremum given by Eq. (20) when $s(\alpha) = s(\beta)$. It is easy to show that this extremum is the maximum, indeed, lying between the two minima at $|A\rangle$ and $|B\rangle$. This trivial connection of two stability conditions in the Points $|A\rangle$ and $|B\rangle$ and the existence of a maximum between them is an illustrative model of occurrence of nonuniqueness of the HF solutions. In this simple frontier molecular orbital model the partial bond order of the frontier orbital $|B\rangle$ [Eq. (25)] has negative value ($P_{12} = -\frac{1}{2}$), but the total bond order in a polyatomic molecule can be positive if all MO's are taken into account. Two different HF solutions giving minima at $|A\rangle$ and at $|B\rangle$ are symmetry adapted solutions. They differ in the number of MO's belonging to the irreducible representation a and b of the symmetry group $(\hat{I}, \hat{T})$. Similar cases of nonuniqueness of the symmetry adapted HF solutions have been found for the alternant hydrocarbons in the PPP model, especially "Kekulé" and "Dewar" type solutions for long polyenes [21, 22]. In this case when the frontier orbitals do not have necessarily the leading role in determining electronic structure (except for almost infinite polyenic chain), the number of MO's which belong to the representation a is the same for "Kekulé" and "Dewar" solutions [22]. Therefore these two solutions cannot be easily interpreted as a ground state and a doubly excited state.

b) If variational parameter $\delta_\alpha = -\delta_\beta = \mathrm{Re}\,\delta$ (i.e. real UHF problem), then the stability condition is:

$$ {}^3E(k\rightarrow\bar{k}) - K_{k\bar{k}} > 0\,. \tag{35}$$

At the Point $|A\rangle$ the *instability* condition in the equivalent orbital representation $|\chi_1\rangle$ and $|\chi_2\rangle$ has the form:

$$ -2\beta' < \Delta + 2K_{12}\,. \tag{336a}$$

The inequality (36a) is equivalent to the existence Condition (21) for the real UHF solution given by Eq. (20) when $s(\alpha) = s(\beta) + 1$ (compare [10]). This UHF solution is a minimum. The corresponding instability condition at the Point $|B\rangle$

$$ 2\beta' < \Delta + 2K_{12} \tag{36b}$$

is always satisfied.

c) If $|\delta_\alpha| = \pm|\delta_\beta| = \mathrm{Im}(\delta)$ (i.e. complex HF problem), then the stability condition takes form:

$$ {}^1E(k\rightarrow\bar{k}) - K_{k\bar{k}} > 0\,. \tag{37}$$

The *instability* conditions at $|A\rangle$ and $|B\rangle$ in equivalent orbitals basis are (compare [20]):

$$ -\beta' < K_{12} \tag{38a}$$

and

$$ \beta' < K_{12}\,. \tag{38b}$$

The Condition (38a) is equivalent to the existence Condition (23) for the complex HF solution Eq. (22), which is a minimum. The RHF and UHF *complex* solutions do not differ in this simple model [compare Eq. (18) with $p = \frac{1}{2}$]. The Condition (38b) is always satisfied for $\beta' < 0$.

6. Overall Behavior of the HF Energy

For the full understanding of the overall behavior of the HF energy for the frontier orbital, it is sufficient to consider the local energy properties of the extremum points described in Section 5. This is easy here because the energy expectation value Eq. (18) is a real quadratic function of only two independent variables.

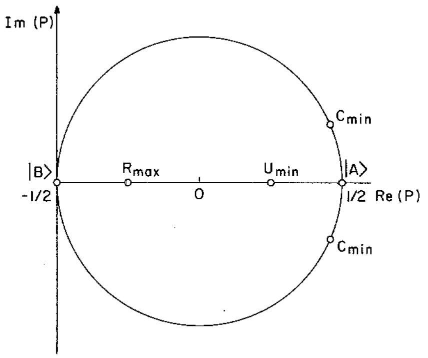

Fig. 1. Schematical picture of the "bond orders" representing the possible stoppings of the interative procedure in the complex plane. Points $|A\rangle$ and $|B\rangle$ correspond to symmetry adapted RHF solutions. $R_{\max}$, $U_{\min}$, and $C_{\min}$ represent the real RHF maximum, real UHF minimum and HF complex solutions, respectively

For the RHF problem $(s(\alpha)=s(\beta))$ and for the UHF problem $(s(\alpha)=s(\beta)+1)$, we label E' [Eq. (18)] as $E_R=E_R\,(|P_{12}|, \mathrm{Re}(P_{12}))$ and $E_U=E_U\,(|P_{12}|, \mathrm{Re}(P_{12}))$, respectively, where $P_{12}=p\exp(i\Phi)$ is a complex variable, which can be interpreted as a RHF or UHF "bond order". The complex "bond order" interval is the part of the complex plane inside the circle with the radius $|P_{12}|=\frac{1}{2}$. The surfaces E_R and E_U in the 3-dimensional space Y [with coordinates $\mathrm{Re}(P_{12})$, $\mathrm{Im}(P_{12})$, and E'] have the common points of the circle $|P_{12}|=\frac{1}{2}$. The Points $|A\rangle$ and $|B\rangle$ which give symmetry adapted energy extrema are in the crossings of the real axis with this circle (Fig. 1).

The Point $|A\rangle$ is a saddle point of the RHF energy surface E_R (in the space Y) if the existence condition for minimum of the complex HF wavefunction is fulfilled Eq. (38a). This saddle point is a maximum in the direction of the imaginary axis and the energy at $|A\rangle$ is higher than at $C_{\min}$ which represents the complex HF solution (Fig. 1). If inequality (38a) is not satisfied, the Point $|A\rangle$ is a minimum.

The Point $|B\rangle$ is a saddle point of E_R if the stability condition of real RHF problem Eq. (34) is satisfied at $|B\rangle$. In this case the energy path from $|A\rangle$ to $|B\rangle$ in the direction of the real axis goes through maximum $R_{\max}$ shown in the Fig. 1 and given by Eq. (20) with $s(\alpha)=s(\beta)$. If inequality (34) is not satisfied $|B\rangle$ is a maximum of E_R.

With respect to the UHF surface E_U, the Point $|A\rangle$ is a maximum if the existence condition for the complex solution Eq. (38a) holds. In that case the inequality (36a) holds always, as well, and gives rise to the real UHF minimum. If Eq. (38a) is not satisfied but Eq. (36a) holds $|A\rangle$ is a saddle point of E_U. If neither of these existence conditions hold, $|A\rangle$ is a minimum of E_U. The point $|B\rangle$ is always maximum of E_U. Therefore, if the existence condition for real UHF minimum (36a) is fulfilled, the energy path from $|A\rangle$ to $|B\rangle$ in the direction of the real axis goes through the absolute minimum $U_{\min}$ of E_U shown in the Fig. 1 and given by Eq. (20) with $s(\alpha)=s(\beta)+1$.

As for the two-orbital model surfaces E_R and E_U have the common points of the circle $|P_{12}|=\frac{1}{2}$, RHF and UHF minima for the complex wavefunction are identical. The general stability conditions derived by Čižek and Paldus [6] show as well, that in the two-dimensional case the singlet and triplet instabilities (i.e.

RHF and UHF instabilities) are the same for variation in direction of the imaginary axis[4]. The complex RHF and UHF minima are not necessarily identical for more complicated models (more than two dimensions), which is indicated by the general form of the stability conditions [6].

The derivative of the UHF energy expression [Eq. (18) for $s(\alpha)=s(\beta)+1$] with respect to the absolute value of the "bond order" $\frac{\partial E'}{\partial p}$ at the Point $C_{\min}$ (cf. Fig. 1) is negative. The Points $C_{\min}$ and $U_{\min}$ on the energy surface E_U are connected by a valley which decreases from $C_{\min}$ to $U_{\min}$ (cf. Fig. 1).

7. Discussion

The appearance of the singlet and triplet excitation energies ${}^1E$ and ${}^3E$ [Eq. (31)] in the stability conditions [Eqs. (32), (35), and (37)] illustrate the importance of magnitude of the energy gap between the highest occupied and the lowest unoccupied molecular orbitals with respect to the ground state configuration. This indicates that the correlation effects are essential for handling these configurations of the closed shell molecules for which the strange HF properties are likely to occur. The connection with the electronic correlation can be also clearly seen if the stability conditions given by Eqs. (32), (35) and (37) are expressed in terms of quantities η and κ which characterize directly the correlation effects:

$$\eta=\frac{2\langle D_A|\hat{H}|D_B\rangle}{\Delta E(A\to B)}=\frac{\Delta}{4|\beta'|}, \tag{39}$$

and

$$\kappa=1-\frac{2\overline{\Delta E}}{\Delta E(A\to B)}=\frac{K_{12}}{|\beta'|}, \tag{40}$$

where $|D_k\rangle$ for $k=A, B$ are Slater determinants [Eq. (3)] with $|\Psi_k^\alpha\rangle=|\Psi_k^\beta\rangle\equiv|k\rangle$ [compare Eqs. (29) and (25)] and

$$\Delta E(A\to B)=\langle D_B|\hat{H}|D_B\rangle-\langle D_A|\hat{H}|D_A\rangle=4|\beta'| \tag{41}$$

is the energy difference between the "doubly excited" configuration D_B and the "ground state" configuration D_A. The symbol $\overline{\Delta E}$ denotes the average value of singlet and triplet excitation energies [Eq. (31)] giving the same weight to singlet and triplet: $\overline{\Delta E}=({}^1E+{}^3E)/2$.

The quantities Δ, K_{12}, and β' (assuming arbitrarily $\beta'<0$) in Eqs. (39) and (40) are molecular integrals defined by Eqs. (12)–(14) expressed in the equivalent orbital basis [Eq. (17)].

The mixing between the closed shell configurations $|D_A\rangle$ and $|D_B\rangle$, which in this simple case means the full configuration depends only on the interaction parameter η [Eq. (39)]. Applicability of Hund's rule for the particular molecular configuration can be measured by the parameter κ. If $\kappa>1$, then $\overline{\Delta E}<0$, i.e. the energy of the triplet state has a lower value than the energy of the singlet state which means that triplet is the lowest state of the molecule (Hund rule).

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[4] The stability conditions resulting from this analysis were first given by Čižek and Paldus [6] and later repeated by Ostlund [28]. Compare also Eq. (35) of Ref. [30]. Some of them have been also obtained by Harris and Falicov [14b].

The stability condition in the framework of the real RHF [cf. Eq. (34)] at the Point $|B\rangle$ having energy higher with respect to the Point $|A\rangle$ indicates the existence of the real RHF maximum and therefore the nonuniqueness of the RHF solutions. This condition can be written in terms of η and κ [Eqs. (39) and (40)] as:

$$\eta > \tfrac{1}{2}(1+\kappa) \tag{42}$$

or

$$2\langle D_A|H|D_B\rangle > \Delta E(A\rightarrow B) - \overline{\Delta E}\,. \tag{42a}$$

The instability condition in the framework of the real UHF approach at the Point $|A\rangle$ given by Eq. (36a) is:

$$\eta > \tfrac{1}{2}(1-\kappa) \tag{43}$$

or

$$2\langle D_A|H|D_B\rangle > \overline{\Delta E}\,. \tag{43a}$$

The existence condition for the complex HF solution [Eqs. (37) and (38a)] can be simply written as:

$$\kappa > 1 \tag{44}$$

or

$$\overline{\Delta E} < 0\,. \tag{44a}$$

In the zero-differential overlap approximation $K_{12}=0$. Therefore, the complex HF solution cannot be obtained at all [compare Eqs. (40) and (44)]. If $K_{12}=0$ the existence conditions [Eqs. (42) and (43)] for the real RHF maximum [Eq. (20): $s(\alpha)=s(\beta)$] and for the real UHF minimum [Eq. (20): $s(\alpha)=s(\beta)+1$] are identical.

For the existence of the complex HF solution, as Eq. (44a) shows, it is necessary that the energy of triplet is lower than the energy of the lowest singlet. Increasing value of κ makes easier existence condition for real UHF minimum [Eq. (43)] to be satisfied and at the same time the occurrence of the real RHF maximum [Eq. (44)] more difficult.

The relatively small energy difference $\Delta E(A\rightarrow B)$ [Eq. (41)] between the two configurations is the necessary condition that the parameters η [Eq. (39)] and κ [Eq. (40)] are large. Such cases are known from the molecular orbital description of the rearrangements of the molecular structures as the orbital energy crossings [29].

According to the inequality (43a) the matrix element $\langle D_A|\hat{H}|D_B\rangle$ determining interaction between Configurations D_A and D_B must be sufficiently large in comparison with the average value of the singly excitation energies $\overline{\Delta E}$ from the Configuration D_A in order that the condition for the UHF minimum is satisfied. Easy occurrence of the UHF minima shows a tendency of spin decoupling. The condition for the RHF maximum (42a) is that the quantity $\langle D_A|H|D_B\rangle$ is larger than half of the difference between the energy of the doubly excited state and the average of the singly excitations from D_A.

It seems that the above discussion can be generalized: Whenever two configurations exist for which the interaction is large (parameter η) the "strange" HF solutions can occur and such molecular configurations show diradical character. This kind of configuration interaction has a distinctly different character from the configuration interaction for the ground state of molecules in the equilibrium geometries. As it is well known in the later case, the correlation energy contains many small contributions from the interactions of the ground state electronic configuration with many excited configurations.

To summarize, the "strange" properties of the HF solutions can be taken as indication of the reactivity for the molecular configurations for which they occur.

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Appendix

Energy Expectation Value for a Slater Determinant

Let us consider a Slater determinant $|D\rangle$ for N electrons constructed from spin orbitals which are eigenfunctions of the operator $\hat{S}_Z$ (compare [27]):

$$\begin{aligned} |D\rangle = (N!)^{\frac{1}{2}} \hat{A} \prod_{j=1}^{N_c} |\psi_j, j\rangle |\alpha, j\rangle |\psi_j, N_c+j\rangle |\beta, N_c+j\rangle \\ \cdot \prod_{l=N_c+1}^{N_c+N_\alpha} |\psi_l, N_c+l\rangle |\alpha, N_c+l\rangle \prod_{s=N_c+N_\alpha+1}^{N-N_c} |\psi_s, N_c+s\rangle |\beta, N_c+s\rangle , \end{aligned} \tag{A 1}$$

where $\hat{A}$ is the antisymmetrizer, N_c is the number of doubly occupied MO's ($|\psi_j, j\rangle$), N_α and N_β are the numbers of singly occupied MO's with α and β spin, respectively.

The projectors on corresponding vector spaces are (compare also [27]):

$$\hat{R}^c = \sum_{j=1}^{N_c} |\psi_j, 1\rangle \langle \psi_j, 1| , \tag{A 2}$$

$$\hat{R}^\alpha = \sum_{j=N_c+1}^{N_c+N_\alpha} |\psi_j, 1\rangle \langle \psi_j, 1| , \tag{A 3}$$

$$\hat{R}^\beta = \sum_{j=N_c+N_\alpha+1}^{N-N_c} |\psi_j, 1\rangle \langle \psi_j, 1| . \tag{A 4}$$

Notice, that $\hat{R}^c \cdot \hat{R}^\lambda = \hat{0}$ for $\lambda = \alpha, \beta$, but $\hat{R}^\alpha \cdot \hat{R}^\beta \neq \hat{0}$. We call the spaces $\mathscr{F}^c$, $\mathscr{F}^\alpha$ and $\mathscr{F}^\beta$ characterized by $\hat{R}^c$, $\hat{R}^\alpha$ and $\hat{R}^\beta$ doubly occupied, α-singly occupied and β-singly occupied Fermi seas, respectively. Using expansion in any arthonormal basis $|\mu\rangle$, the expectation value of the Hamiltonian

$$\hat{H} = \sum_{j=1}^{N} \hat{h}(j) + \sum_{j<k}^{N} \hat{g}(j, k) \tag{A 5}$$

takes the form (compare Eq. (6) of Ref. [27]):

$$\begin{aligned} E = \langle D| \hat{H} |D\rangle &= \tfrac{1}{2} \sum_{\mu,\nu=1}^{M} P_{\mu\nu}^{T} h_{\mu\nu} + \tfrac{1}{2} \sum_{\mu,\nu=1}^{M} (P_{\mu\nu}^{T\alpha} F_{\mu\nu}^{\alpha} + P_{\mu\nu}^{T\beta} F_{\mu\nu}^{\beta}) \\ &= \sum_{\mu,\nu=1}^{M} P_{\mu\nu}^{T} h_{\mu\nu} + \tfrac{1}{4} \sum_{\mu,\nu,\varrho,\sigma} (\mu\varrho | \nu\sigma) [2 P_{\mu\sigma}^{T} P_{\nu\varrho}^{T} - P_{\mu\varrho}^{T} P_{\nu\sigma}^{T} - P_{\mu\varrho}^{-} P_{\nu\sigma}^{-}] \end{aligned} \tag{A 6}$$

where

$$h_{\mu\nu} = \langle \mu, 1| h(1) |\nu, 1\rangle , \tag{A 7}$$

$$(\mu\nu | \varrho\sigma) = \langle \mu, 1| \langle \varrho, 2| \hat{g}(1, 2) |\nu, 1\rangle |\sigma, 2\rangle , \tag{A 8}$$

$$P_{\mu\nu}^{T\lambda} = \langle \nu| \hat{R}^c + \hat{R}^\lambda |\mu\rangle , \quad \lambda = \alpha, \beta , \tag{A 9}$$

$$P_{\mu\nu}^{T} = \langle \nu| 2\hat{R}^c + \hat{R}^\alpha + \hat{R}^\beta |\mu\rangle = P_{\mu\nu}^{T\alpha} + P_{\mu\nu}^{T\beta} , \tag{A 10}$$

$$P_{\mu\nu}^{-} = P_{\mu\nu}^{T\alpha} - P_{\mu\nu}^{T\beta} , \tag{A 11}$$

and

$$F_{\mu\nu}^{\lambda} = h_{\mu\nu} + \sum_{\varrho,\sigma} \{P_{\varrho\sigma}^{T} [(\mu\nu | \varrho\sigma) - \tfrac{1}{2}(\mu\sigma | \varrho\nu)] \mp \tfrac{1}{2} P_{\varrho\sigma}^{-} (\mu\nu | \varrho\sigma)\} . \tag{A 12}$$

In Eq. (A 12) upper and lower sign corresponds to $\lambda = \alpha$ and β, respectively. Vectors of the used orthonormal basis are labeled by μ, ν, ϱ, σ.

Using expansion of one electron function $|j\rangle$ in orthonormal basis $|\mu\rangle$

$$|j\rangle = \sum_{\mu} |\mu\rangle \langle\mu|j\rangle = \sum_{\mu} c_{j\nu} |\mu\rangle \tag{A 13}$$

bond order matrix elements of the Eqs. (A 9) and (A 10) can be written:

$$P^{\mathscr{F}}_{\mu\nu} = \sum_{j\in\mathscr{F}} m_j c^{*}_{j\mu} c_{j\nu}\,, \tag{A 14}$$

where $\mathscr{F}$ can be doubly occupied $\mathscr{F}^{c}$ or α-singly occupied $\mathscr{F}^{\alpha}$ or β-singly occupied $\mathscr{F}^{\beta}$-Fermi sea with corresponding occupation number m_j.

References

1. Thouless, D. J.: The quantum mechanics of many-body systems. New York: Academic Press 1961
2. a) Adams, W. H.: Phys. Rev. **127**, 1650 (1962)
2. b) Hibbert, A., Coulson, C. A.: J. Phys. B **2**, 458 (1969)
3. Löwdin, P. O.: Rev. Mod. Phys. **35**, 496 (1963); Advan. Chem. Phys. **14**, 283 (1969)
4. Stanton, R. E.: J. Chem. Phys. **48**, 257 (1968)
5. King, H. F., Stanton, R. E.: J. Chem. Phys. **50**, 3789 (1969)
6. Čižek, J., Paldus, J.: J. Chem. Phys. **47**, 3976 (1967); **53**, 821 (1970)
7. Paldus, J., Čižek, J.: J. Chem. Phys. **52**, 2919 (1970); J. Polymer Sci. **28**, 199 (1970)
8. Coulson, C. A., Fischer, I.: Phil. Mag. **40**, 386 (1949)
9. Overhouser, A. W.: Phys. Rev. Letters **4**, 115, 462 (1960)
10. Koutecký, J.: J. Chem. Phys. **46**, 2443 (1967)
11. Kaplan, T. A., Kleiner, W. H.: Phys. Rev. **156**, 1 (1967)
12. Fenton, E. W.: Phys. Rev. Letters **21**, 1427 (1968)
13. Kruglyak, Yu. H., Ukrainskii, I. I.: Intern. J. Quantum Chem. **4**, 57 (1970)
14. a) Fukutome, H.: Progr. Theoret. Phys. (Kyoto) **40**, 998, 1227 (1968)
14. b) Harris, R. A., Falicov, L. M.: J. Chem. Phys. **50**, 4590 (1969); **51**; 5034 (1969)
14. c) For the critical discussion of the papers a) and b) see: Paldus, J., Čižek, J.: Progr. Theoret. Phys. (Kyoto) **42**, 769 (1969); Paldus, J., Čižek, J.: J. Chem. Phys. **53**, 1619 (1970)
15. a) Cazes, D., Salem, L., Tric, C.: J. Polymer Sci. (Part C) **29**, 109 (1970)
15. b) Tric, C.: J. Polymer Sci. **29**, 119 (1970)
16. Harris, F. E.: J. Chem. Phys. **43**, 517 (1965)
17. Brändas, E.: J. Mol. Spectry. **27**, 236 (1968); Intern. J. Quantum Chem. **1**, 847 (1967); **2**, 37 (1968); **2**, 793 (1968)
18. Coulson, C. A., White, R. J.: Mol Phys. **18**, 577 (1970)
19. Larson, E. G.: Intern. J. Quantum Chem. **2**S, 83 (1968)
20. Pople, J. A.: Intern. J. Quantum Chem. **5**S, 175 (1971)
21. Koutecký, J., Bonačić, V.: Chem. Phys. Letters **10**, 401 (1971)
22. Bonačić, V., Koutecký, J.: J. Chem. Phys. **56**, 4563 (1972)
23. Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951)
24. Koutecký, J., Bonačić, V.: J. Chem. Phys. **55**, 2408 (1971)
25. Bonačić, V., Koutecký, J.: Intern. J. Quantum Chem. **5**S, 137 (1971)
26. Koutecký, J., Bonačić-Koutecký, V.: Theoret. Chim. Acta (Berl.) **36**, 163 (1975)
27. Koutecký, J., Bonačić-Koutecký, V.: Chem. Phys. Letters **15**, 558 (1972)
28. Ostlund, N. S.: J. Chem. Phys. **57**, 2994 (1972)
29. See e.g.: Buenker, R. Y., Peyerimhoff, S. P.: J. Phys. Chem. **73**, 1299 (1969); Hayes, E. F.: J. Chem. Phys. **51**, 4787 (1969); Newton, M. D., Schulman, J. M.: J. Am. Chem. Soc., **94**, 4391 (1972); Stohrer, W.-D., Hoffmann, R.: J. Am. Chem. Soc. **94**, 779 (1972)
30. Paldus, J., Čižek, J.: Phys. Rev. A **2**, 2268 (1970)

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