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

## II. Analysis of the Customary Iterative Procedure

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The commutator relation between the Hartree-Fock matrix and the one-electron density matrix in Fukui's frontier molecular orbital model has been used to investigate the various kinds of ending of the customary iterative SCF procedure. Step by step description of the iterative SCF procedure has been given in an illustrative graphical way. There is a close connection among the symmetry nonadapted RHF solution for symmetrical molecules, the UHF solution for the closed shell molecules, the complex HF solution and the occurrence of oscillation for the iterative procedure. It has been explicitly shown that the nonconvergence of the usual iterative procedure occurs when the Coulombic interaction between not fully coupled spins of the molecular systems with a certain amount of diradical character is sufficiently weak. The results of the analysis concerning the properties of the Hartree-Fock approach are generalized for the asymmetrical molecules.

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

## 1. Introduction

Besides the strange Hartree-Fock solutions (symmetry non-adapted-RHF, UHF and complex solutions) discussed in details in the first contribution of this series [1], another obvious failure of the one-electron approximation is the nonconvergence of the usual iterative procedure. In some cases even when the artificial recipes for enforcing the convergence work, the description of the molecular properties based on the HF solution can be doubtful. It has been already demonstrated [2, 3] that the strange properties of the HF approach like nonconvergence, often interpreted as consequences of the computational difficulties, have on the contrary physical reason. The connection between the convergence difficulties and the strange HF solutions is evident because of their frequent occurrence for the molecular configurations characterized by the small energy gap between the highest occupied and the lowest unoccupied MO's.

The aim of this paper is to study this connection, as well as the specific conditions for the presence of various irregularities, when the customary iterative

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procedure is used. This should complete the attempt to characterize the degree of the opening of closed shell for the molecular configurations according to the occurrence of the HF strange properties.

The detailed analysis of the customary iterative procedure [4] for solving the HF problem is carried out on the frontier orbital model (cf. [5]). This very simple model can reveal some important and general features which in more sophisticated models might not be realized due to the very complicated nature of the HF problem. The strange features of the SCF method, when met in the computational practice can be easily misinterpreted without such an analysis. The connection between the physical and mathematical side of the one-electron approach can also help to choose the appropriate method for treating the correlation effects in a way that the chemically interesting properties of unstable molecular systems can be qualitatively well described.

## 2. Commutator of the Hartree-Fock Matrix and Bond Order Matrix in the Representation of the Equivalent Orbitals

The solving of the HF eigenequations is *exactly* equivalent to finding the one-electron density matrix or the bond order matrix, which commutes with the HF matrix (compare Eqs. (A9) and (A10), and for proof see Eqs. (A1)–(A8) as well as Refs. [6–8]):

$$[\boldsymbol{F}^{\lambda}(\boldsymbol{P}^{T\alpha}, \boldsymbol{P}^{T\beta}), \tilde{\boldsymbol{P}}^{T\lambda}] = 0 \tag{1}$$

where $\lambda = \alpha, \beta$ labels spin. The matrices in Eq. (1) are in the representation of an orthonormal basis $|\varrho\rangle$. The Hartree-Fock matrix elements for the two-dimensional basis are given by Eqs. (A13) and (A14) and for the general case by Eq. (A12) of Ref. [1]. The bond order matrix elements can be written:

$$P_{\mu\nu}^{T\lambda} = \sum_{j \in (\mathscr{F}^c \oplus \mathscr{F}^\lambda)} C_{j\mu}^* C_{j\nu},\ \lambda = \alpha, \beta\,, \tag{2}$$

where $\mathscr{F}^c$ and $\mathscr{F}^\lambda$ are doubly and singly $-\lambda$ occupied Fermi seas [compare Eq. (A14) of Ref. [1] and $C_{j\varrho}$ are expansion coefficients from Eq. (A5)].

The nonlinear problem formulated by Eq. (1) is usually solved by the iterative SCF procedure [4], where the matrix elements of the HF operator $\hat{F}^{\lambda}[n]$ in the $n$-step of the procedure are built by bond order matrices from the $[n-1]^{\text{st}}$ step $\boldsymbol{P}^{T\alpha}[n-1]$ and $\boldsymbol{P}^{T\beta}[n-1]$ (cf. [3]):

$$[\boldsymbol{F}^{\lambda}[n]\,(\boldsymbol{P}^{T\alpha}[n-1], \boldsymbol{P}^{T\beta}[n-1]), \tilde{\boldsymbol{P}}^{T\lambda}[n]] = 0\,. \tag{3}$$

Such a formulation of the iterative procedure has a closed and compact form, which makes it possible to analyse the convergence criteria of the iterative procedure as well as the influence of various constraints. The main emphasis of this study is put of course on the stopping of the iterative procedure, which occurs when the individual terms of the left hand side of Eq. (3) are not any more step-dependent. The stopping is not a sufficient condition for ending of the iterative process in the *solution of the* HF *problem*, which is equivalent to Eq. (1). Therefore, we study various kinds of terminating of the iterative procedure which can be RHF, UHF, complex HF solutions *or* ending in *oscillations without convergence.*

We consider in the main part of the paper (with exception of Section 5) molecules with the symmetrical framework of nuclei, but without apriori assumption upon the symmetry properties of the electronic structure. The seemingly inconsequent assumption makes possible to follow the mechanism which gives rise to the "pathological" properties of the HF iterative procedure. If for symmetrical molecules the symmetry assumptions upon spin or space properties of the one-electron density are introduced in the zero-step, then of course, only rounding errors during the iterative procedure can give rise to these "pathological" properties. As emphasized in the Introduction, the motivation of this work is not in the investigation of the computational side of the problem but to characterize the molecular configurations by means of possible occurrence of the HF strange properties.

When the frontier molecular orbitals of a symmetrical molecule have a decisive role in the HF iterative procedure, then Eq. (3) in the two-dimensional representation of equivalent orbitals can be used. Equivalent orbitals are defined as one-electron functions, which under symmetry operation $\hat{T}(\hat{T}^2=\hat{I})$ transform as:

$$|\chi_2\rangle = \hat{T}|\chi_1\rangle \tag{4}$$

and vice versa (cf. Eq. (17) of Ref. [1]). The bond order matrix elements $P^{T\lambda}_{\mu\nu}$ given by Eqs. (A11) and (A12) depend on the step of iterative procedure $[n]$ through independent variables $p_\lambda[n]$, $\Phi_\lambda[n]$ and integers $s(\lambda, n)$. Matrix elements of the HF operator Eqs. (A13) and (A14) now in the equivalent orbital basis enter Eq. (3). The off-diagonal matrix element of the commutation Relation (3) is:

$$[\boldsymbol{F}^\lambda[n], \tilde{\boldsymbol{P}}^{T\lambda}[n]]_{12}=0$$

or

$$\begin{aligned}&p_\lambda[n]\exp(-i\Phi_\lambda[n])\,(-1)^{s(\lambda,n)+s(\lambda,n-1)}\{(-1)^{s(\bar{\lambda},n-1)+s(\lambda,n-1)}\\&\cdot\Delta D_{\bar{\lambda}}[n-1]+(K_{12}-\gamma_{12})\,D_\lambda[n-1]\}-D_\lambda[n]\,\{\beta'+2K_{12}p_{\bar{\lambda}}[n-1]\cos\Phi_{\bar{\lambda}}[n-1]\\&+(K_{12}-\gamma_{12})\exp(-i\Phi_\lambda[n-1])\}=0\,.\end{aligned} \tag{5}$$

The diagonal element of the commutation Relation (3) is:

$$[\boldsymbol{F}^\lambda[n], \tilde{\boldsymbol{P}}^{T\lambda}[n]]_{11}=0$$

or

$$\begin{aligned}&\{\beta'+2K_{12}P_{\bar{\lambda}}[n-1]\cos\Phi_{\bar{\lambda}}[n-1]\}\sin\Phi_\lambda[n]\\&\quad-(K_{12}-\gamma_{12})\,p_\lambda[n-1]\sin(\Phi_\lambda[n-1]-\Phi_\lambda[n])=0\,.\end{aligned} \tag{6}$$

If $\lambda=\alpha, \beta$, then $\bar{\lambda}=\beta, \alpha$. In Eq. (5) the following symbols are used:

$$D_\lambda[m]=\sqrt{1-4\,p_\lambda^2[m]} \tag{7}$$

and

$$\Delta=\gamma-\gamma_{12}\,. \tag{8}$$

Definitions of molecular integrals are given by Eqs. (A17)–(A20) taking into account that for a symmetrical molecule the following relations among the molecular integrals in the equivalent orbital basis hold: $\gamma_{11}=\gamma_{22}\equiv\gamma$ and $(11/12)=(22/21)$ [cf. Eqs. (A17), (A19), and (A20)].

## 3. Commutator Relations Describing the Iterative SCF Procedure and its Stopping

The stopping of the iterative procedure takes place when the invidual terms in Eqs. (5) and (6) are not any more step-dependent, i.e.

$$p_\lambda[n] = p_\lambda[n-1], |\cos \Phi_\lambda[n]| = |\cos \Phi_\lambda[n-1]$$

and

$$s(\alpha, n) + s(\beta, n) = s(\alpha, n-1) + s(\beta, n-1)\,. \tag{9}$$

The lengthy analysis shows that the stopping of the procedure requires $|\cos \Phi_\alpha| = |\cos \Phi_\beta| \equiv |\cos \Phi|$ and $p_\alpha = p_\beta \equiv p$. The energy extrema $\frac{\partial E}{\partial p_\lambda} = \frac{\partial E}{\partial \Phi_\lambda} = 0$ fulfill the same conditions (cf. Section 4 of Ref. [1]). Therefore, we consider the whole procedure itself with these limitations.

When the stopping Condition (9) are introduced, the Eq. (6) for the diagonal commutator matrix element and the imaginary part of the offdiagonal commutator matrix element (5) are compatible only for particular parametrization, or if $p = \frac{1}{2}$. Therefore, we examine for the real Slater determinant only the real part of the offdiagonal matrix element of the commutator (5) which means that $\sin \Phi = 0$, i.e. $\cos \Phi = \pm 1$. On the other hand, for the complex Slater determinant only the diagonal commutator matrix element (6) *with* $p = \frac{1}{2}$ must be analysed, because the case of particularly required parametrization is of no importance.

Then the real part of Eq. (5) can be written in a simple form:

$$C[n-1]\, B[n-1]\, (-1)^{s(\lambda,n) + s(\lambda,n-1)} = C[n]\, A[n-1]\,, \tag{10}$$

where

$$C[m] = D[m]/P[m]\,, \tag{11}$$

$$P[m] = p[m] \cos \Phi[m] = p[m]\, \tau[m],\ \tau[m] = \pm 1\,, \tag{12}$$

$$B[n-1] = (-1)^{s(\alpha,n-1) + s(\beta,n-1)}\, \Delta + K_{12} - \gamma_{12}\,, \tag{13}$$

and

$$A[n-1] = 3K_{12} - \gamma_{12} + \beta'/p[n-1]\, \tau[n-1]\,. \tag{14}$$

The real RHF and UHF approaches differ only in the assumption upon $s(\alpha, n-1)$ and $s(\beta, n-1)$. The RHF method requires that

$$s(\alpha, n-1) = s(\beta, n-1) \tag{15}$$

The UHF approach is basically free of constraints upon the one-electron density matrix, but for the UHF solution it holds (cf. Ref. [1]):

$$s(\alpha, n-1) = s(\beta, n-1) + 1\,. \tag{16}$$

The iterative procedure is determined when $A$, $B$, and $C$ Eqs. (11), (13), and (14) are not any more step-dependent. Then Eq. (10) is satisfied if $C = 0$, i.e. $p = \frac{1}{2}$, which is the end of the allowed "bond order" interval [cf. for definition Eqs. (A 11) and (A 12)] *or* if

$$B(-1)^{s(\lambda,n) + s(\lambda,n-1)} = A\,. \tag{17}$$

The sum of integers $s(\lambda, n) + s(\lambda, n-1)$ connects two successive steps of the iterative procedure. The relative magnitude of "atomic or group charges" in two successive steps $[n-1]$ and $[n]$ is determined by these two integers $s(\lambda, n-1)$ and $s(\lambda, n)$ [compare Eq. (A 11)].

When the stopping of the iterative procedure is achieved, the Hartree-Fock solutions are obtained only for $s(\lambda, n) = s(\lambda, n-1)$, because only then the whole one-electron density matrix is not step dependent:

$$\boldsymbol{P}^{T\lambda}[n] = \boldsymbol{P}^{T\lambda}[n-1] \equiv \boldsymbol{P} . \tag{18}$$

If $s(\lambda, n) = s(\lambda, n-1) + 1$ when the iterative procedure is terminated according to Eq. (9), the procedure ends in the oscillations of diagonal elements of the one-electron density matrix, although the "bond order" is step independent, and no convergence is achieved: if $s(\lambda, n) = s(\lambda, n-1) + 1$ and $P_{jj}^{T\lambda}[n-1] > P_{\bar{j}\bar{j}}^{T\lambda}[n-1]$, then $P_{jj}^{T\lambda}[n] < P_{\bar{j}\bar{j}}^{T\lambda}[n]$ ($j = 1, 2; \bar{j} = 2, 1$) [cf. Eq. (A 11)].

This statement in the representation of equivalent orbitals does not exclude the possibility that in the LCAO representation of a polyatomic molecule the oscillation between nondiagonal elements of the bond order matrix can occur, as well.

The iterative procedure for the complex Slater determinant can be studied using Eq. (6) with $p = \frac{1}{2}$ in the form:

$$\operatorname{cotg} \Phi[n] = A'[n-1] \operatorname{cotg} \Phi[n-1] \tag{19}$$

where

$$A'[n-1] = \frac{1}{K_{12} - \gamma_{12}} \left[ 3K_{12} - \gamma_{12} + \frac{2\beta'}{\cos \Phi[n-1]} \right] . \tag{20}$$

The conditions for stopping of the iterative process for the complex wavefunction are

$$A'[n-1] = A'[n] \equiv A' = \pm 1 . \tag{21}$$

The above discussion of Eqs. (10) and (17) shows explicitly that the self consistency does not have to be achieved always, even when the individual terms of the commutator relations are step independent. This is a consequence of the nonequivalence of the commutator Relation (1) (defining the solution of the HF problem) and the commutator relation (3) (describing the iterative procedure) in the limit $n \to \infty$.

## 4. Step by Step Investigation of the Iterative SCF Procedure

It is always possible to assume that $C[n] \neq 0$ [Eq. (11)] before ending the iterative procedure for the real Slater determinant. Therefore, Eq. (10) can be written in the form useful for the investigation of the iterative process:

$$J[n, n-1] = G[n-1] . \tag{22}$$

The left- and right-hand side of Eq. (22) are:

$$\begin{aligned} J[n, n-1] &= \frac{C[n-1]}{C[n]} (-1)^{s(\lambda,n)+s(\lambda,n-1)} \\ &= \frac{\sqrt{x^2[n-1]-4}}{\sqrt{x^2[n]-4}} \; \frac{\tau[n]}{\tau[n-1]} (-1)^{s(\lambda,n)+s(\lambda,n-1)} \end{aligned} \tag{23}$$

where

$$x[m]=1/p[m] \tag{24}$$

and

$$G[n-1]=\frac{A[n-1]}{B[n-1]}=a+bx[n-1], \tag{25}$$

where

$$a=(3K_{12}-\gamma_{12})/[(-1)^{s(\alpha,n-1)+s(\beta,n-1)}\,\Delta+K_{12}-\gamma_{12}] \tag{26}$$

and

$$b=\beta'\tau[n-1]/[(-1)^{s(\alpha,n-1)+s(\beta,n-1)}\,\Delta+K_{12}-\gamma_{12}]. \tag{27}$$

Equation (22) describes the iterative procedure for the real wavefunction without *a priori* symmetry assumptions in a very simple way because the right-hand side $G[n-1]$ (Eq. 25) is a linear function in the inverse absolute value of the "bond order" in the $[n-1]^{\text{st}}$ step ($p^{-1}[n-1]=x[n-1]$). The values of integrals in Eqs. (26) and (27) and the assumption upon positive or negative "bond order" in $[n-1]^{\text{st}}$ step ($\tau[n-1]=\pm 1$, Eq. (12)) determine slopes of these straight lines. The left-hand side of Eq. (22) $J[n,n-1]$ [Eq. (23)] connects the values of the "bond orders" in two successive steps in such a way that the ending of the iterative procedure occurs if $|J[n,n-1]|=1$. We assume throughout that $\Delta>2K_{12}$ which describes reasonable localization for equivalent orbitals.

The iterative procedure for the complex Slater determinant can be studied using Eq. (19) devided by cotg $\Phi[n-1]$ if cotg $\Phi[n-1]\neq 0$. The detailed analysis of the iterative procedure with the help of graphical presentation will be given for the real Slater determinant. The analysis for the complex Slater determinant can be made along the same lines.

### 4.1. *The* RHF *Approach for the Real Slater Determinant*

The RHF constraint $s(\alpha,n)=s(\beta,n)\equiv s[n]$ [Eq. (15)] implies that constants $a$ and $b$ from the definition of the function $G[n-1]$ [Eqs. (26) and (27)] are:

$$a=(3K_{12}-\gamma_{12})/(\gamma-2\gamma_{12}+K_{12}) \tag{28}$$

and

$$b=\beta'\tau[n-1]/(\gamma-2\gamma_{12}+K_{12}). \tag{29}$$

a) If the following relation for the molecular integrals holds:

$$\gamma-2\gamma_{12}+K_{12}<0 \tag{30}$$

then $a>1$ [Eq. (28)] and $b\gtrless 0$ [Eq. (29)] according to $\beta'\tau[n-1]\lessgtr 0$. The inequality (30) is fulfilled when the Coulombic interaction between the equivalent orbitals of the frontier orbital model is relatively large.

For illustration the representatives of the straight lines of $G[n-1]$ are given in Fig. 1a where $x[n-1]>2$ is the interval of the allowed "bond orders". In the figures of this section we take arbitrarily $\beta'<0$.

b) If the inequality

$$\gamma-2\gamma_{12}+K_{12}>0 \tag{31}$$

holds, then $b\gtrless 0$ [Eq. (29)] according to $\beta'\tau[n-1]\gtrless 0$ and the constant a [Eq. (28)] can lie in two different intervals:

ba) if

$$\gamma - 3\gamma_{12} + 4K_{12} > 0\,, \tag{32}$$

then $-1 < a < 0$ and

bb) if

$$\gamma - 3\gamma_{12} + 4K_{12} < 0 \tag{33}$$

then $a < -1$. The inequalities (31), especially (32) indicate weak Coulombic interaction between the equivalent orbitals. The examples of $G[n-1]$ for the Cases ba) and bb) are given in Fig. 1 b.

The points of interest are crossings $x_1, x_0$, and $x_{-1}$ of the straight line $G[n-1]$ with the horizontals $1, 0, -1$ in Fig. 1a and b. Whether these crossings exist or not depends on the Slope b [Eq. (29)] of $G[n-1]$, i.e. on the values of the molecular integrals. The iterative procedure is quantitatively described in Fig. 1, while the qualitative character of the procedure in various "bond order" intervals, as well as the various possibilities of its stopping is shown in Fig. 2.

The existence conditions for "bond order" $P_m$ with $m = 1, 0, -1$ (Fig. 2) in the mentioned points of interest $x_1, x_0, x_{-1}$ (Fig. 1) obtained from Eq. (25) for $G[n-1]\,(x_m) = m$ are:

$$-\frac{1}{2} < P_1 = \tau[n-1]/x_1 = 1/x'_1 = \frac{\beta'}{\Delta - 2K_{12}} < \frac{1}{2} \tag{34}$$

$$-\frac{1}{2} < P_0 = \tau[n-1]/x_0 = 1/x'_0 = \frac{\beta'}{\gamma_{12} - 3K_{12}} < \frac{1}{2}\,, \tag{35}$$

$$-\frac{1}{2} < P_{-1} = \tau[n-1]/x_{-1} = 1/x'_{-1} = \frac{\beta'}{3\gamma_{12} - \gamma - 4K_{12}} < \frac{1}{2}\,. \tag{36}$$

The existence Condition (34) is equivalent to the existence condition for the real RHF maximum (21) (Ref. [1]).

As already mentioned, the function $J[n, n-1]$ [Eq. (23)] describes two successive steps of the iterative procedure. It connects the absolute values of the "bond orders" $p[n]$ and $p[n-1]$, their signs $\tau[n]$ and $\tau[n-1]$ and the relative magnitudes of "atomic charges" [cf. Eq. (A 11)] through integers $s[n]$ and $s[n-1]$. The qualitative summary of the information obtained from function $J$ [Eq. (23)] is given in Fig. 2.

For the analysis of the function $J$ it is advantageous to introduce the quantity $\sigma[n, n-1]$ [cf. Eq. (23)]

$$\sigma[n, n-1] = \frac{\tau[n]}{\tau[n-1]}(-1)^{s[n]+s[n-1]}\,. \tag{37}$$

If $\sigma[n, n-1] = 1$ it follows that either both signs of the "bond order" and relative magnitudes of "atomic charges" do not change from $[n-1]^{\text{st}}$ to $[n]^{\text{th}}$ step, or both do change. If $\sigma[n, n-1] = -1$ either the sign of the "bond order" changes from the $[n-1]^{\text{st}}$ to the $[n]^{\text{th}}$ step: $\tau[n] = -\tau[n-1]$, and $s[n] = s[n-1]$, or oscillation of "atomic charges" occurs: $s[n] = s[n-1] + 1$, but the "bond order" does not change the sign through the steps: $\tau[n] = \tau[n-1]$. We introduce the constraint $\tau[n] = \tau[n-1]$ in the graphs of Fig. 2 (as well as throughout Section 4)

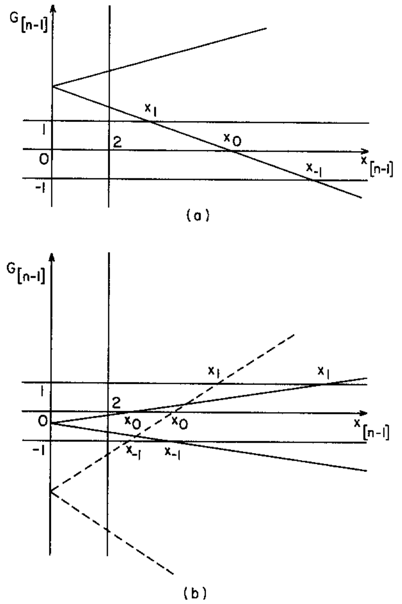

Fig. 1a and b. Schematic plots of the function $G_{[n-1]}$ [Eq. (25)] for the real RHF problem. Points $x_0, x_1$, and $x_{-1}$ are defined by Eqs. (34)–(36). (a) Inequality (30) is fulfilled. (b) Full lines – inequalities (31) and (32) fulfilled, broken lines – inequalities (31) and (33) fulfilled

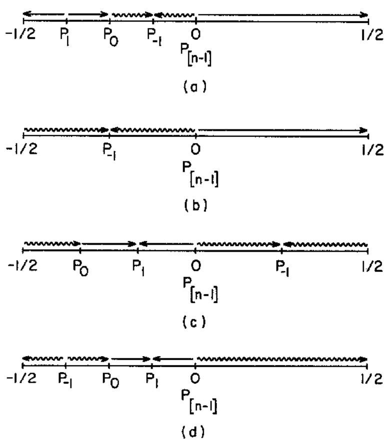

Fig. 2a–d. "Bond order" intervals for the real RHF procedure. $P_0, P_1, P_{-1}$ are defined by Eqs. (34)–(36). The straight and wiggled lines assigned to the intervals with $\sigma[n, n-1] = 1$ and $\sigma[n, n-1] = -1$, respectively [Eq. (37)]. The arrows oriented to the right and to the left indicate intervals of $P_{[n-1]}$ for which $P_{[n]} > P_{[n-1]}$ and $P_{[n]} < P_{[n-1]}$, respectively. (a) and (b) examples when inequality (30) holds ($P_1 < P_0 < P_{-1} < 0$) with $P_1 > -\frac{1}{2}$ and $P_0 < -\frac{1}{2}$, respectively. (c) Example when inequalities (31) and (32) hold ($P_0 < P_1 < 0 < P_{-1}$) with $P_0 > -\frac{1}{2}$ and $P_{-1} < \frac{1}{2}$. (d) Example, when inequalities (31) and (33) hold ($P_{-1} < P_0 < P_1 < 0$) with $P_{-1} > -\frac{1}{2}$

in order to visualize easier the iterative procedure. This constraint means that there is no switching between positive and negative values of the "bond order" in two successive steps of the iterative procedure. The maintained sign of the "bond order", i.e. the fixed irreducible representation throughout the iterative procedure is not the only possible criterium for choosing the occupied MO's. Their choice can be made according to the molecular orbital energy criterium as well, which will be discussed in Section 6. If the "bond order" sign is fixed, then the straight lines in Fig. 2 denote no changes in relative magnitudes of "atomic charges" in the $[n-1]^{\text{st}}$ and the $[n]^{\text{th}}$ step and the wiggled lines indicate oscillations of the "atomic charges". The "bond order" in the $[n]^{\text{th}}$ step $P[n]$ does not necessarily have to lie in the same interval $(P_m, P_m')$ as the "bond order" in the $[n-1]^{\text{st}}$ step $P[n-1]$ (where $P_m$ and $P_m'$ are defined by Eqs. (34)–(36)). Therefore, the iterative procedure does not in general have to end with the "bond order" value pointed out by an arrow of the particular interval in which $P[n-1]$ lies. The ending of the iterative procedure during which the "jumping" between the "bond order" intervals occurs, can be followed in details with the help of the graphical presentation of Eq. (22) similar to that of Fig. 1.

According to this analysis three types of ending the iterative procedure by fulfilling Eq. (9) are possible:

a) Approaching towards the ends of the "bond order" interval $(-\frac{1}{2}, \frac{1}{2})$. The values of the "bond order" $P = \pm\frac{1}{2}$ correspond to the HF solutions $C=0$ of Eq. (10), which are symmetry adapted normal "nonpathological" RHF solutions. Compare the HF energy extreme in Ref. [1], listed under a) of Section 4.

b) The stopping of the iterative procedure at the point $P_1 = \dfrac{\beta'}{\Delta - 2K_{12}}$ [Eq. (34)] is the solution of Eq. (17) for $s[n] = s[n-1]$ and corresponds to the energy extremum described in Ref. [1] as the Case b) of Section 4 (cf. Eq. (20) with $s[\alpha] = s[\beta]$). This HF extremum is the maximum of the energy expectation value according to the discussion in Section 6 of Ref. [1].

Even when in our oversimplified frontier orbital model the frontier orbital "bond order" $P_1$ is negative, the overall "bond orders" of a polyatomic molecule can be positive. Then, if the iterative procedure is directed by the frontier orbitals, the HF solution can be in reality a maximum without being noticed.

c) Stopping at the point $P_{-1} = \dfrac{\beta'}{3\gamma_{12} - \gamma - 4K_{12}}$ [Eq. (36)] is the solution of Eq. (17) for $s[n] = s[n-1] + 1$, and *does not* correspond to any extremum of the energy expectation value. The ending of the iterative procedure at $P_{-1}$ is manifested in oscillations of the "atomic charges", i.e. no convergence is achieved (cf. [3] and [4]).

### *4.2. The* UHF *Approach for the Real Slater Determinant*

The iterative procedure for the UHF approach $(s(\alpha, n) = s(\beta, n) + 1)$, [Eq. (16)] can be described by Eqs. (22)–(27) with

$$a = \frac{\gamma_{12} - 3K_{12}}{\gamma - K_{12}} \tag{38}$$

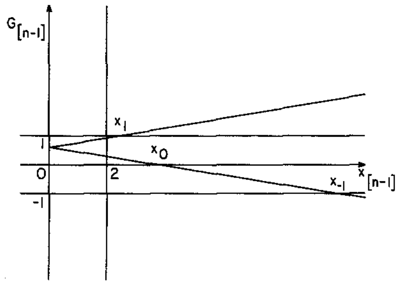

Fig. 3. Schematic plots of the function $G_{[n-1]}$ for the real UHF problem. Points $x_0$, $x_1$, $x_{-1}$ are defined by Eqs. (40)–(42)

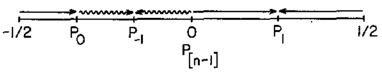

Fig. 4. The "bond order" intervals for the real UHF procedure. $P_0$, $P_1$, $P_{-1}$ are defined by Eqs. (40)–(42). An example when $P_1 < \frac{1}{2}$ and $P_0 > -\frac{1}{2}$ is given. The further description is the same as in Fig. 2

and

$$b = \frac{-\beta'\tau[n-1]}{\gamma - K_{12}}. \tag{39}$$

In the UHF method, constant a [Eq. (38)] can lie only in the interval (0, 1). Therefore, the presentation of the iterative process by the straight lines $G[n-1]$ Eq. (25) is very simple as shown in Fig. 3. The qualitative description of the iterative process is presented in Fig. 4. The existence conditions for the "bond order" $P_m$ in Fig. 4 with $m = 1, 0, -1$ at the points $x_1, x_0, x_{-1}$ are:

$$-\frac{1}{2} < P_1 = \frac{\tau[n-1]}{x_1} = \frac{-\beta'}{\Delta + 2K_{12}} < \frac{1}{2}, \tag{40}$$

$$-\frac{1}{2} < P_0 = \frac{\tau[n-1]}{x_0} = \frac{\beta'}{\gamma_{12} - 3K_{12}} < \frac{1}{2}, \tag{41}$$

$$-\frac{1}{2} < P_{-1} = \frac{\tau[n-1]}{x_{-1}} = \frac{\beta'}{\gamma + \gamma_{12} - 4K_{12}} < \frac{1}{2}. \tag{42}$$

The intervals with the straight lines indicate no changes in the relative magnitude of the spin charges from the $[n-1]^{\text{st}}$ to the $[n]^{\text{th}}$ step of the procedure, and the wiggled lines suggest oscillations of spin charges in two successive steps. In the UHF method oscillations of spin charges do not imply, of course, oscillations of overall "atomic charges".

The iterative procedure in the UHF approach assuming the stopping Conditions (9) can end with the following values of the "bond order" $P$ [Eq. (12)]:

a) Approaching the symmetry adapted RHF solution $P = \frac{1}{2}$ if the existence condition for $P_1$ [Eq. (40)] is not satisfied and if the sign of the "bond order" is assumed to be positive. The existence condition for $P_{-1}$ is probable to be satisfied for the usual values of the molecular integrals. In this case the iterative procedure with fixed negative "bond order" can end at the symmetry adapted solution $P = -\frac{1}{2}$ only with hitting it directly.

b) Stopping of the iterative procedure at the Point $P_1$ if the existence Condition (40) holds. The Point $P_1$ being always positive represents the UHF minimum which is given in the Ref. [1] by Eq. (20) with $s(\alpha) = s(\beta) + 1$.

c) Ending at the Point $P_{-1}(<0)$ [if Eq. (42) holds] does not represent the solution of the UHF problem. The iterative procedure ends in oscillations of the spin charges from step to step with overall "atomic charges" invariant.

### 4.3. Concluding Remark

The use of the extrapolation techniques forcing convergence of the SCF procedure for unstable molecules can lead to the HF solution lying in the energy surface region which is far away from the starting point and therefore not well understood. The safest way of avoiding convergence difficulties is to estimate the zero step of the iterative procedure sufficiently near to the meaningful HF solution. The difficulty is that the safe convergence region can be very small. In the simplest symmetrical frontier orbital model the convergence region is a single Point $P = \frac{1}{2}$ or $-\frac{1}{2}$. The symmetry constraints can be considered as a special case of the zero step estimate for the MO's applicable, of course, only for symmetrical molecules.

## 5. The Real Restricted Iterative Procedure for the Slightly Asymmetrical Molecule

It is easy to show that the main features of the iterative procedure analysis carried out on the frontier orbital model for a symmetrical molecule remain mutatis mutandis unchanged for a slightly asymmetrical molecule. The small asymmetry can be caused by deviation from the equilibrium geometry or by the asymmetrical substitution in the periphery of the molecule with the symmetrical functional group. As already discussed in the case of a symmetrical molecule, the symmetry constraints assumed in the 0th step of the iterative procedure can eliminate some strange characteristics of the HF approach as ending in the HF maximum or ending in oscillations of the "atomic charges". When symmetry constraints are not applicable, like in the case of a slightly asymmetrical molecule, the described strange features cannot be avoided by symmetry constraints.

For the description of the slightly asymmetrical molecule we use the frontier orbital model where frontier orbitals are linear combinations of two approximately localized vectors. These vectors are assumed to deviate only slightly from the equivalent orbitals of the corresponding symmetrical molecule [cf. Eq. (4)]. For a diatomic molecule in a minimal basis set these localized functions would be simply atomic orbitals.

In the frontier orbital model of a polyatomic molecule the slight asymmetry is introduced through the assumption upon molecular integrals: $h_{11} - h_{22} \neq 0$ [Eq. (A 15)], $\gamma_{11} - \gamma_{22} \neq 0$ [Eq. (A 17)] and $Z \neq 0$ [Eq. (A 20)], where the deviations from zero are small quantities. We use the matrix element of the commutator $[\boldsymbol{F}[n], \boldsymbol{P}[n]] = 0$ for the investigation of the stopping of the real RHF ($\boldsymbol{P}^{T\alpha}[n] = \boldsymbol{P}^{T\beta}[n] \equiv \boldsymbol{P}[n]$ and $\boldsymbol{F}^{\alpha}[n] = \boldsymbol{F}^{\beta}[n] \equiv \boldsymbol{F}[n]$) iterative procedure. Substitution of Eqs. (A 11)–(A 14) and (12) in this matrix element gives rise to:

$$\begin{aligned}\{1 - x'_0 P[n-1]\}\, D'[n] = {} & P[n]\, D'[n-1]\, (x'_0 - x'_{-1}) + \Lambda' P[n] \\ & + \frac{Z'}{2} \{4P[n]\, P[n-1] - D'[n]\, D'[n-1]\}\end{aligned} \tag{43}$$

where

$$\Lambda' = [h_{11} - h_{22} + \tfrac{1}{2}(\gamma_{11} - \gamma_{22})]/\beta' \tag{44}$$

and

$$Z' = Z/\beta' . \tag{45}$$

The molecular integrals are defined in the Appendix 2 [Eqs. (A 15)–(A 20)]. The quantities $x'_m$ with $m = 1, 0, -1$ are given by Eqs. (34)–(36) and

$$D'[m] = (-1)^{s[m]} (1 - 4p^2[m])^{\frac{1}{2}} = (-1)^{s[m]} D[m] \tag{46}$$

(compare also Eq. (7)).

Let us assume that, in general, for the asymmetrical molecule the iterative process can end not only with oscillations of "atomic charges", but also with oscillations of the "bond orders". The possibility of ending of the iterative procedure in the oscillation of the "bond orders" (i.e. off-diagonal elements of the one-electron density matrix) for a symmetrical molecule can also be shown by relatively lengthy analysis.

We make the assumption that for big enough $[n]$ the following expressions hold:

$$P[2n-1] = \bar{P} + \delta , \tag{47}$$

$$P[2n] \quad = \bar{P} + \varepsilon , \tag{48}$$

where $\delta$ and $\varepsilon$ are small quantities. Therefore, Eq. (43) in the $[2n-1]^{\text{st}}$ and in the $[2n]^{\text{th}}$ step can be written:

$$\begin{aligned}& U(\bar{P}, s[2n] + s[2n-1])\, D_0 - \delta x'_0 D_0 + W(\bar{P}, s[2n] + s[2n-1], \delta, \varepsilon) \\ & \quad = (-1)^{s[2n]} V(\bar{P}, s[2n] + s[2n-1])\end{aligned} \tag{49}$$

and

$$\begin{aligned}& U(\bar{P}, s[2n] + s[2n-1])\, D_0 - \varepsilon x'_0 D_0 + W(\bar{P}, s[2n] + s[2n-1], \varepsilon, \delta) \\ & \quad = (-1)^{s[2n-1]}\, V(\bar{P}, s[2n] + s[2n-1] ,\end{aligned} \tag{50}$$

respectively, where

$$U(\bar{P}, s[2n] + s[2n-1]) = 1 - \bar{P}[x'_0 - (-1)^{s[2n]+s[2n-1]} (x'_{-1} - x'_0)] , \tag{51}$$

$$\begin{aligned}W(\bar{P}, s[2n] + s[2n-1], \delta, \varepsilon) = {} & -\delta x'_0 D_0 - \frac{4\varepsilon\bar{P}}{D_0}(1 - x'_0 \bar{P}) \\ & + (x'_{-1} + x'_0)\, (-1)^{s[2n]+s[2n-1]} \left\{\varepsilon D_0 - \frac{4\delta P^2}{D_0}\right\} ,\end{aligned} \tag{52}$$

$$V(\bar{P}, s[2n] + s[2n-1]) = \Lambda' \bar{P} + \frac{Z'}{2} [4\bar{P}^2 - (-1)^{s[2n]+s[2n-1]} (1 - 4\bar{P}^2)] , \tag{53}$$

and

$$D_0 = (1 - 4\bar{P}^2)^{\frac{1}{2}} . \tag{54}$$

The only difference between the left hand sides of Eqs. (49) and (50) consists in exchanging the role of the "bond order" deviations $\delta$ and $\varepsilon$ in the function $W$. In the zero-approximation with respect to $Z'$, $A'$, $\varepsilon$, and $\delta$ (i.e. for a corresponding symmetrical molecule) the value of $\bar{P}$ is determined either by $D_0 = 0$ [cf. Eq. (54)] describing the symmetry adapted solutions or by $U(\bar{P}, s[2n] + s[2n-1]) = 0$ [cf. Eq. (51)] giving the other possibilities of ending the iterative procedure: the ending in the RHF maximum ($\bar{P} = P_1$ for $s[2n] = s[2n-1]$) or in the oscillations of the "atomic charges" ($\bar{P} = P_{-1}$ for $s[2n] = s[2n-1] + 1$).

From the comparison of Eqs. (49) and (50) follows, if $s[2n] = s[2n-1]$ and therefore $P = P_1$, that $\varepsilon = \delta$. Then, the iterative procedure ends with the "bond orders" giving the HF maxima for the slightly asymmetrical molecule (see the remark [9]):

$$P_{\max}(s) = P[2n] = P[2n-1] = P_1[1 - (-1)^s \, V(P_1, 0)/D_0]\,, \tag{55}$$

where

$$V(P_1, 0) = A'P_1 - \frac{Z'}{2}(1 - 8P_1^2)\,. \tag{56}$$

The "bond order" $P_{\max}$ can yield two according to the choice of the even or odd value of now step independent integer $s$. The even or odd value of the integer $s$ describes two possible choices of "atomic or group charges" [cf. Eq. (A11)]. In the asymmetrical case two atoms or atomic groups are distinguishable and, therefore, $P_{\max}(1)$ and $P_{\max}(2)$ ($P_{\max}(1) + P_{\max}(2) = 2P_1$) can appear giving different energy values.

If $s[2n] = s[2n-1] + 1$ and therefore $\bar{P} = P_{-1}$, from the comparison of Eqs. (49) and (50) follows that $\varepsilon = -\delta$. The iterative procedure ends with oscillations between $P[2n]$ and $P[2n-1]$[1]:

$$P[2n] = P_{-1} + (-1)^{s[2n]} \, V(P_{-1}, 1)\, D_0/[(P_1)^{-1} - 4P_{-1}]\,, \tag{57}$$

and

$$P[2n-1] = 2P_{-1} - P[2n]\,, \tag{58}$$

where

$$V(P_{-1}, 1) = A'P_{-1} + Z'/2\,. \tag{59}$$

Oscillations between $P[2n]$ and $P[2n-1]$ occur according to Eq. (58) around the Point $P_{-1}$. This point describes for a symmetrical molecule the ending of the iterative procedure with oscillations of "atomic charges" [cf. Eq. (36)]. In the asymmetrical case oscillations of "atomic charges" and of the "bond orders" in two successive steps are connected. The energy expectation value in even and odd steps of the iterative procedure are, of course, different.

## 6. Selection of MO's in the Slater Determinant According to their Energies

In the preceding Sections the sign of the frontier orbital "bond order" has been taken as fixed throughout the iterative procedure. This recipe is useful for investigation of SCF procedures when the study of the region of molecular orbital

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[1] In the derivation of Eqs. (55) and (57) it is assumed that the second term is a small quantity. This is, of course, the condition for ending the expansion in $\varepsilon$ and $\delta$ after first order in Eqs. (49) and (50).

crossing is of interest. The Slater determinants. in the frontier orbital model giving rise to the positive or negative frontier orbital "bond order" simulate the Slater determinants with the highest occupied MO's belonging to the irreducible representation $a$ and $b$, respectively of the two-dimensional symmetry group $(\hat{I}, \hat{T})$ [cf. Eq. (4)]. The selection of molecular orbitals according to the irreducible representations is the usual recipe for the iterative SCF procedure when the region of the molecular orbital crossing is investigated.

On the other hand the generally used SCF techniques choose the MO's entering the Slater determinant according to the order of increasing MO energies. For analysing the iterative procedure with the MO energy criterium, it is adadvantageous to consider the secular equations in the $[n]^{\text{th}}$ step corresponding to the two-dimensional HF problem. Then the MO energies for the real RHF approach $(\boldsymbol{F}^{T\alpha}[n] = \boldsymbol{P}^{T\beta}[n] \equiv \boldsymbol{P}[n])$ obtained explicitly from the secular determinant are:

$$\varepsilon_{1,2}[n] = (F_{11}[n] + F_{12}[n])/2 \mp |F_{12}| \left[ 1 + \frac{(F_{22}[n] - F_{11}[n])^2}{4|F_{12}[n]|} \right]^{\frac{1}{2}}$$

and the following relation for the "bond order" corresponding to $\varepsilon_1[n]$ and $\varepsilon_2[n]$ according to the upper and lower sign holds:

$$P[n]/P_{11}[n] = \omega[n] \mp \operatorname{Sign}(F_{12}[n])\,(1 + \omega^2[n])^{\frac{1}{2}}\,, \tag{61}$$

where

$$P[n] \equiv P_{12}[n]\,,$$

and

$$\omega[n] = (F_{22}[n] - F_{11}[n])/2\,F_{12}[n]\,. \tag{62}$$

From Eq. (61) it is evident that

$$\begin{aligned} \operatorname{Sign}(P[n]) &= \mp \operatorname{Sign}(F_{12}[n]) = \mp \operatorname{Sign}\{\beta' - (\gamma_{12} - 3K_{12})\,\tau[n-1]\,p[n-1]\} \\ &= \mp \operatorname{Sign}(\beta') \operatorname{Sign}\left\{1 - \frac{P[n-1]}{P_0}\right\} \end{aligned} \tag{63}$$

where $P_0$ is defined by Eq. (35). We assume again arbitrarily that $\beta' < 0$. Then $P_0$ is always negative.

For the lower MO energy $\varepsilon_1[n]$ [upper sign in Eq. (64)] from Eqs. (61) and (63) follows that if $P[n-1] > 0$ then the "bond order" in the following step of the iterative procedure is also positive: $P[n] > 0$. If the "bond order" in the $[n-1]^{\text{st}}$ step is negative the "bond order" in the $[n]^{\text{th}}$ step can be negative or positive: if $P[n-1] < 0$ and if $-\frac{1}{2} < P[n-1] < P_0 < 0$ then $P[n] < 0$, but if $-\frac{1}{2} < P_0 < P[n-1] < 0$ then $P[n] > 0$. In order to illustrate the behaviour of the iterative procedure with the MO energy selection criterium we can use Fig. 2 allowing now, of course, the change of the "bond order" sign during the process.

If the inequality (30) for the molecular integrals is satisfied (Fig. 2a and b) then according to the analysis of this section the iterative procedure ends in the symmetry adapted solution with $P = \frac{1}{2}$ if $P_0 < P[0] < 0$ and of course for any $P[0] > 0$. The iterative procedure will end with the symmetry adapted solution $P = -\frac{1}{2}$ if $P_1$ [Eq. (34)] exists and $P[0] < P_1 < P_0$. If the existence Condition (35) for $P_0$ is fulfilled $(2|\beta'| < (\gamma_{12} - 3K_{12}))$ the occupied molecular orbital with the negative "bond order" exhibits lower MO energy $\varepsilon_b$ than the corresponding virtual orbital belonging to the irreducible representation $a(\varepsilon_a - \varepsilon_b = 2\beta' + \gamma_{12} - 3K_{12})$.

For the weak spin coupling when the inequalities (31) and (32) hold and the existence condition for $P_{-1}$ [Eq. (36)] is satisfied, then the iterative procedure starting from any positive or negative "bond order" in the $[0]^{\text{th}}$ step $P[0]$ always ends in the oscillations of the "atomic charges" without convergence (cf. Fig. 2c), (if, of course, the symmetry adapted solution is not hitted in the $[0]^{\text{th}}$ step). If the Point $P_{-1}$ does not exist, the only possible ending of the iterative procedure is the symmetry adapted HF solution with $P=\frac{1}{2}$. If the inequalities (31) and (33) are fulfilled (cf. Fig. 2d), then the symmetry adapted HF solution with $P=\frac{1}{2}$ is obtained, when $P_{-1}<P[0]<0$ and of course for any $P[0]>0$. If the Point $P_{-1}$ exists and $P[0]<P_{-1}<0$, then the iterative procedure ends with the symmetry adapted solution with $P=-\frac{1}{2}$.

For the higher MO energy $\varepsilon_2[n]$ [lower sign in Eq. (60)] the following conclusions concerning the "bond orders" in two successive steps can be drawn:

If $P_0<P[n-1]$, then $P[n]<0$.

If $-\frac{1}{2}<P[n-1]<P_0$, then $P[n]>0$.

We consider again examples for the higher MO energy $\varepsilon_2[n]$ on Fig. 2 (real RHF approach) allowing the change of the "bond order" sign. In case that Point $P_0$ [Eq. (35)] does not lie in the allowed "bond order" interval, then the iterative procedure must end in the following way: Either in oscillations with the "bond order" $P_{-1}<0$, when the inequality (30) holds (Fig. 2b) or in the HF maximum with the "bond order" $P_1<0$ if the inequality (31) holds (cf. Fig. 2c and d) independently of whether the starting "bond order" $P[0]$ is positive or negative. If the point $-\frac{1}{2}<P_0<0$ exists and $P[n]\in(-\frac{1}{2},P_0)$, it is not excluded that the iterative process will continue switching between the positive and negative frontier "bond orders" values from step to step. As it can be noticed from this discussion, if the SCF solution with frontier molecular orbital in the Slater determinant having higher MO energy $\varepsilon_2[n]$ [Eq. (60)] is looked for, the SCF iterative procedure exhibits especially strange features.

The above analysis shows that in the molecular orbital crossing region, when the iterative procedure uses the energy criterium for the selection of the occupied MO's, the convergence difficulties are even more likely to occur.

## Conclusion

1. The existence condition for nonconvergence [Eq. (36), when inequalities (31) and (32) hold] in the terms of the correlation parameters $\eta$ and $\kappa$ can be formulated as:

$$\eta>\tfrac{1}{2}(1-\kappa)+\tfrac{1}{2}(\Gamma-\kappa)\,. \tag{64}$$

The quantities $\eta=(2\langle D_A|\hat{H}|D_B\rangle)/\Delta E(A\to B)$ and $\kappa=1-2\overline{\Delta E}/\Delta E(A\to B)$ (cf. Eqs. (39)–(41) of Ref. [1]) measure the interaction between the configurations $D_A$ and $D_B$ and the relative position of the lowest singlet and triplet, respectively. The symbol $\Gamma$ is defined as:

$$\Gamma=\frac{\gamma_{12}}{|\beta'|}=\frac{4\gamma_{12}}{\Delta E(A\to B)} \tag{65}$$

$\Delta E(A \to B)$ is the energy difference between the doubly excited configuration $D_B$ and the ground state configuration $D_A$. The Slater determinants $D_A$ and $D_B$ are built by the symmetry adapted frontier molecular orbitals belonging to the irreducible representations $a$ and $b$ of the symmetry group $(\hat{I}, \hat{T})$ (cf. Eqs. (24) and (25) and the Discussion of Ref. [1]). $\overline{\Delta E}$ is the average value between the singlet and triplet excitation energies. The Condition (64) for nonconvergence in the interval of the positive "bond orders" differs from the condition of occurrence of the UHF minimum $(\eta > \frac{1}{2}(1-\kappa)$ [Eq. (43) of the Ref. [1]) only in the term $\frac{1}{2}(\Gamma - \kappa)$, which is practially determined by the values of the Coulombic integral $\gamma_{12}$ measured, of course, in the units of $\Delta E(A \to B)$. At the molecular orbital energy crossing i.e. for $|\beta'| = 0$, the existence condition for the RHF maximum $((\gamma - \gamma_{12} + 2K_{12}) > 0)$ and for the triplet instability $((\gamma - \gamma_{12} - 2K_{12}) > 0)$ are always satisfied. The condition for the nonconvergence at the crossing point is $\gamma - 3\gamma_{12} + 4K_{12} > 0$ which requires very weak Coulombic interaction between the equivalent orbitals [i.e. inequality (32) is fulfilled]. The nonconvergence of the customary iterative procedure can be added to the strange HF solutions as another symptom of the diradical character when the Coulombic interaction between the nonpaired electrons is weak.

2. The investigation of the unstable molecular configurations with the SCF method should be carried out with extreme care, especially when the electronic configurations with higher energies are considered. It is explicitly shown that the iterative procedure can end in the HF maximum without being noticed or in the oscillations of the "atomic charges" and/or "bond orders" depending on the zero step assumptions and on the way of selection of the MO's into the Slater determinant throughout the procedure.

3. It has been explicitly shown on the example of the slightly asymmetrical molecule that the introduction of the asymmetry does not change the strange features of the HF problem. Evidently, these HF properties can be met even more frequently for the slightly asymmetrical molecules where the symmetry constraints cannot be applied.

## Appendix

### *1. Projector on the Space Spanned by Eigenvectors of a One-Electron Operator*

From eigenequation for any one-electron operator $\hat{B}$ follows:

$$\hat{B}|j\rangle = \varepsilon_j |j\rangle, \tag{A 1}$$

$$[\hat{B}, \hat{R}^{(j)}] = 0, \tag{A 2}$$

where $\hat{R}^{(j)}$ is a projector operator

$$\hat{R}^{(j)} = |j\rangle\langle j|. \tag{A 3}$$

Equations (A 2) holds for any linear combination of $\hat{R}^{(j)}$ i.e.

$$\sum_{j \in \mathscr{E}} \hat{R}^{(j)} m_j = \hat{R}^{(\mathscr{E})}, \tag{A 4}$$

where $\mathscr{E}$ is any subspace of the space spanned by the complete set of eigenvector $|j\rangle$ of Eq. (A 1). If $m_j^2 = m_j$ for all $j \in \mathscr{E}$, then $\hat{R}^{(\mathscr{E})}$ is a projector, as well.

In the representation of orthonormal basis $|\varrho\rangle$

$$|j\rangle = \sum_{\varrho} |\varrho\rangle\langle\varrho|j\rangle = \sum_{\varrho} C_{j\varrho}|\varrho\rangle \tag{A 5}$$

commutator given by Eq. (A2) takes form

$$[\boldsymbol{B}, \tilde{\boldsymbol{P}}^{\mathscr{E}}] = 0\,, \tag{A6}$$

where

$$\tilde{\boldsymbol{P}}^{\mathscr{E}} = \boldsymbol{R}^{\mathscr{E}}\,, \tag{A7}$$

and

$$P^{\mathscr{E}}_{\varrho\nu} = \sum_{j \in \mathscr{E}} m_j \cdot C^*_{j\varrho} C_{j\nu}. \tag{A8}$$

$\tilde{\boldsymbol{P}}$ is the transposed matrix to $\boldsymbol{P}$.

### *2. Commutator of the* HF *Matrix and One-Electron Density Matrix*

In the RHF approach the $\alpha$- and $\beta$-singly occupied Fermi seas $\mathscr{F}^\alpha$ and $\mathscr{F}^\beta$ are empty ($\hat{R}^\alpha = \hat{R}^\beta = 0$ compare Eqs. (A3) and (A4) of Ref. [1]) and in the UHF approach doubly occupied Fermi sea $\mathscr{F}^C$ is empty ($\hat{R}^C = 0$ compare Eq. (A3) of Ref. [1]). One-electron functions in the Slater determinant (Eq. (A1) of Ref. [1]) for which energy expectation value $E$ (Eq. (A6) of Ref. [1]) exhibits extremum are in both RHF and UHF methods eigenfunctions of the operator $\hat{F}^\lambda$, $\lambda = \alpha, \beta$ (Eq. (A12) of Ref. [1]). As operator $\hat{F}^\lambda$ can be in both approaches considered as a function of $P^{T\lambda}_{\mu\nu} = \langle \mu | \hat{R}^C + \hat{R}^\lambda | \nu \rangle$ (Eq. (A9) of Ref. [1]), commutator given by Eq. (A6) takes form:

$$[\boldsymbol{F}^\lambda(\boldsymbol{P}^{T\alpha}, \boldsymbol{P}^{T\beta}), \tilde{\boldsymbol{P}}^{\mathscr{E}}] = 0\,. \tag{A9}$$

Space $\mathscr{E}$ can be in general spanned by any manifold of vectors which are eigenvectors of the HF operator $\hat{F}^\lambda$. We can take $\mathscr{E} = \mathscr{F}^C \oplus \mathscr{F}^\lambda$, i.e. for RHF: $\mathscr{E} \equiv \mathscr{F}^C$ and for UHF: $\mathscr{E} \equiv \mathscr{F}^\lambda$. In this case

$$\boldsymbol{P}^{\mathscr{E}} = \boldsymbol{P}^{T\lambda}\,. \tag{A10}$$

As $\boldsymbol{P}^{T\lambda}$ is a representation of a projector, which is idempotent by definition, the one electron density matrix in the two-dimensional orthonormal basis can be written as:

$$P^{T\lambda}_{jj} = \tfrac{1}{2}\left(1 \mp (-1)^{s(\lambda)+j} \sqrt{1 - 4p^2_\lambda}\right), \quad j = 1, 2\,, \tag{A11}$$

and

$$P^{T\lambda}_{12} = p_\lambda \exp(i\Phi_\lambda)\,, \tag{A12}$$

where $s(\lambda)$ is an integer (compare Eqs. (6) and (7) of Ref. [1]). In these considerations the connection between the restricted and unrestricted version of the HF method is emphasized. It is therefore, advantageous to use the quantity $P_{12} = P^{T\alpha}_{12} = P^{T\beta}_{12}$ as the definition of the "bond order" for RHF, as well. The customary definition of the "bond order" is: $2P_{12} = P^{T\alpha}_{12} + P^{T\beta}_{12}$. Matrix elements of the Hartree-Fock operator $F^\lambda$ (compare Eq. (A12) of Ref. [1]) in the representation of the two-dimensional orthonormal basis $|\mathscr{E}\rangle$ are:

$$\begin{aligned} F^\lambda_{\mu\mu} = {} & h_{\mu\mu} + \tfrac{1}{2}(\lambda_{\mu\mu} + 2\gamma_{12} - K_{12}) - [(\gamma_{\mu\mu} - \gamma_{12})/2]\,(-1)^{s(\lambda)+\mu} \sqrt{1 - 4p^2_{\bar{\lambda}}} \\ & + [(\gamma_{12} - K_{12})/2]\,(-1)^{s(\lambda)+\mu} \sqrt{1 - 4^2_{\bar{\lambda}}} + 2(\mu\mu|\mu\bar{\mu})\, p_\lambda \cos \Phi_{\bar{\lambda}}, \quad \lambda = \alpha, \beta;\ \mu = 1, 2\,, \end{aligned} \tag{A13}$$

$$F^\lambda_{12} = \beta' - (\gamma_{12} - K_{12})\, p_\lambda \exp(-i\Phi_\lambda) + 2K_{12}\, p_{\bar{\lambda}} \cos \Phi_{\bar{\lambda}} + \tfrac{1}{2} Z (-1)^{s(\bar{\lambda})} \sqrt{1 - 4p^2_{\bar{\lambda}}}\,. \tag{A14}$$

If $\lambda = \alpha$ then $\bar{\lambda} = \beta$ and vice versa. If $\mu = 1$ then $\bar{\mu} = 2$ and vice versa. The molecular integral in Eqs. (A13) and (A14) are defined as:

$$h_{\mu\nu} = \langle \mu, 1 | \, h(1) \, | \nu, 1 \rangle\,, \tag{A15}$$

$$(\mu\nu | \varrho\sigma) = \langle \mu, 1 | \, \langle \varrho, 2 | \, \hat{g}(1, 2) \, | \nu, 1 \rangle \, | \sigma, 2 \rangle\,, \tag{A16}$$

$$\gamma_{\mu\nu} = (\mu\mu | \nu\nu)\,, \tag{A17}$$

$$K_{12} = \langle 12 | 12 \rangle\,, \tag{A18}$$

$$\beta' = h_{12} + \tfrac{1}{2}[(11|12) + (22|21)]\,, \tag{A19}$$

$$Z = (11|12) - (22|21)\,. \tag{A20}$$

Operator $\hat{h}(1)$ and $\hat{g}(1, 2)$ are one- and two-electron operators of the effective Hamiltonian (Eq. (10) of Ref. [1]).

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