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Ab initio Hartree-Fock Instabilities in Closed-Shell Molecular Systems

Gilberte Chambaud, Bernard Levy and Philippe Millie

Laboratoire de Chimie, ENSJF, E.R.A. 470, 1, rue M. Arnoux, F-92120 Montrouge, France

The Hartree-Fock instability of twelve polyatomic systems is studied at the *ab initio* level. It is found that all the systems with at least one double bond, exhibit a non-singlet instability. On the other hand instabilities of singlet type as well as instabilities of non-real type appear only in a small number of cases. The existence of these instabilities is discussed with respect to the location of low-lying excited states and to the weight of ionic structure.

Key words: Hartree-Fock instabilities

1. Introduction

Our purpose is to detect instabilities in some particular and favourable molecular systems at the *ab initio* level.

The molecular orbitals φ_i given by the Hartree-Fock method are obtained by assuming that the Slater determinant Φ_0 constructed from these φ_i's correspond to a stationary point of the energy function,

$$\partial^{(1)}E=0 \tag{1}$$

Generally a few constraints are imposed on the φ_i's, namely:

- th φ_i's transform as the irreducible representations of the symmetry point group of the system (symmetry constraint);
- the φ_i's are either doubly or singly occupied (spin-constraint);
- the φ_i's are real (except, possibly, for some orbitals belonging to multi-dimensional representations of high symmetry point groups where a complex form may be more convenient).

These constraints are introduced in order to simplify the numerical calculation.

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But it may happen that the determinant thus obtained (or restricted Hartree-Fock determinant Φ_{RHF}) corresponds to an energy higher than the energy of the Slater determinant obtained without any constraint (or unrestricted Hartree-Fock determinant Φ_{UHF}). After Löwdin [7], such a case is called a symmetry dilemma.

Moreover, some physical properties of the systems may be hidden by the constraints introduced in the calculation: for instance, the alternation of the bond lengths in the conjugated polyenes can be interpreted by the fact that the bond orders in the UHF function [8–10] are themselves alternating, even when the bond lengths are kept all identical in the calculation. In contrast, the RHF wave function (determined with all lengths identical) yields bond orders that are all equal and consequently no indication of bond alternation is apparent.

Many studies have been made by semiempirical calculations[1] on the existence of a UHF function with a lower energy than the RHF one. On the other hand, *ab initio* studies have been made for atomic systems, for instance O^{2-} [16, 17], but not for molecules (see however Refs. [18, 19]).

The study we undertook is limited by the following considerations:

1) We considered only the so-called Hartree-Fock instability, excluding the study of a local minimum. Particularly we have never tried, in the case where no instability is found, to determine whether it is the absolute minimum or a local one. And in the case where an instability is found we have neither tried (with the exception of F_2) to determine an actual minimum. In other words, our results are concerned only with local properties of the energy surface $E(\Phi)$ and not with the whole of the surface.

2) We considered only systems with an even number of electrons and closed-shell RHF wavefunctions.

2. Theory

We begin by a brief summary of the theory of Hartree-Fock instability. The general formulation of the instabilities has been given by Thouless [20] and in the density matrix formalism by Adams [21]. The distinction between the different cases of instability is due to Čižek and Paldus [12].

Let Φ_{RHF} be the SCF restricted function of a system, and φ_i one orbital of Φ_{RHF}. The constraint can be eliminated by a variation of φ_i of the form:

$$\varphi_i \longrightarrow \varphi'_i = \varphi_i + \sum_l \varphi_l u_{li} \tag{2}$$

where φ_l is a virtual orbital and u_{li} a coefficient giving the amplitude of the variation.

Considering the nature of the constraints imposed in the Φ_{RHF} function calculation, the first-order variations of the energy with respect to the u'_{li}'s are zero in a closed-shell system (this is a consequence of the Brillouin theorem for any mixture of two

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[1] Most of them are described in the series of papers published by Koutecký, and by Čižek and Paldus in the last ten years; see Refs. [11–15] and references quoted therein.

orbitals φ_l and φ_i whatever their spin and symmetry properties may be) and so the second-order variations of the energy is to be taken into account.[2]

Thus our problem, if the second-order variations of the energy are positive for every possible choice of the u'_{li}'s:

$$\left.\frac{\partial^2 E}{\partial u_{li}^2}\right\}_{\Phi_{\mathrm{RHF}}} > 0$$

the energy cannot decrease in the vicinity of Φ_{RHF} and then Φ_{RHF} is said to be "stable".

Of course, stability and instability are purely local properties: the latter involves the existence of a Φ_{UHF} with a lower energy, in the vicinity of Φ_{RHF}. On the contrary, if the Φ_{RHF} is stable, it may happen that, in the u'_{li}'s space, the energy increases in the nearest vicinity of Φ_{RHF} and then decreases and tends to another minimum: that can be called a situation of double well. This problem has not been studied here, because there is no easy way to detect it: it implies a very long calculation process because each point of the whole surface $E=f(\Phi)$ has to be tested.

According to Thouless [20] and Paldus and Čižek [12], the second-order variation of the energy, with respect to the u'_{li}'s can be written in the following quadratic form:

$$\partial^2 E = \frac{1}{2}\begin{pmatrix} D \\ \overline{D} \end{pmatrix}^{+} \begin{pmatrix} A & B \\ \overline{B} & \overline{A} \end{pmatrix} \begin{pmatrix} D \\ \overline{D} \end{pmatrix} \tag{3}$$

(D) is the column matrix of the u'_{li}'s, $(\overline{D})$ is the complex conjugate of (D), and (A) and (B) are square matrices defined by:

$$A_{li,kj} = \langle \varphi_l | f | \varphi_k \rangle\, \delta_{ij} - \langle \varphi_i | F | \varphi_j \rangle\, \delta_{kl} + (li, jk) - (lk, ji)$$
$$B_{li,kj} = (li, kj) - (lj, ki)$$

F is the Fock operator corresponding to Φ_{RHF}, and

$$(li, jk) = \int \overline{\varphi}_l(1)\varphi_i(1)\overline{\varphi}_j(2)\varphi_k(2)\,\frac{1}{r_{12}}\, d\tau_1\, d\tau_2$$

(i and j denote the occupied orbitals, and k and l the virtual orbitals).

According to (3), the detection of instability reduces to a diagonalization: if all the eigenvalues of the matrix:

$$E'' = \begin{vmatrix} A & B \\ \overline{B} & \overline{A} \end{vmatrix}$$

are positive, all the second-order variations of the energy at the RHF point are positive and Φ_{RHF} is stable. On the other hand, if one or several eigenvalues are

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[2] For open-shell systems, the consequences of the Brillouin theorem are not the same as in closed-shell systems and some of the first-order variations are not zero. Consequently, it is always possible to assert that, in a radical system, a UHF function with a lower energy than the RHF one, exist without considering the second-order variations of the energy.

negative, Φ_{RHF} is unstable and the corresponding eigenvectors suggest a starting direction towards a lower energy.

If Φ_{RHF} is a real and closed-shell determinant, the eigenvalues of E'' can be classified in three types. In order to do that, it is convenient to make the following transformation on the u'_{li}'s.

$$\begin{aligned} u^{s}_{li} &= (u_{l\alpha,\, i\alpha} + u_{l\beta,\, i\beta}) 1/\sqrt{2} \\ u^{t_1}_{li} &= (u_{l\alpha,\, i\alpha} - u_{l\beta,\, i\beta}) 1/\sqrt{2} \\ u^{t_2}_{li} &= (u_{l\beta,\, i\alpha} - u_{l\alpha,\, i\beta}) 1/\sqrt{2} \\ u^{t_3}_{li} &= (u_{l\beta,\, i\alpha} - u_{l\alpha,\, i\beta}) i/\sqrt{2} \end{aligned} \tag{5}$$

where $u_{i\alpha,\, l\alpha}$ describes the mixture of the spin orbital $\varphi_i \cdot \sigma(\alpha)$ and the spin orbital $\varphi_l \cdot \sigma(\alpha)$.

Furthermore, one may notice that the eigenvectors D of E'' are eigenvectors of either the $(A+B)$ matrix or the $(A-B)$ matrix, consequently one has three types of instability.

2.1. *Instabilities of the First Type* (*Singlet Instabilities*)

The corresponding eigenvalues of E'' are obtained by diagonalizing the matrix

$$\begin{aligned} E''^{s} &= A^{s} + B^{s} \\ A^{s}_{li,\, kj} &= \langle \varphi_l | F | \varphi_k \rangle\, \delta_{ij} - \langle \varphi_i | F | \varphi_j \rangle\, \delta_{kl} + 2(li, jk) - (lk, ji) \\ B^{s}_{li,\, kj} &= 2(li, jk) - (lj, ik) \end{aligned} \tag{6}$$

The eigenvectors of E'' are real and are associated to the u^{s}_{li}.

The corresponding variations of the Φ_{RHF} function are real and preserve the closed-shell nature of the function. Such variations are particularly interesting if they destroy the symmetry properties occurring when φ_l and φ_i belong to different symmetry representations.

2.2. *Instabilities of the Second Type* (*Non-Singlet or Triplet*)

The corresponding eigenvalues of E'' are obtained by diagonalizing the matrix

$$E''^{t} = A^{t} + B^{t} \tag{7}$$

$$\begin{aligned} A^{t}_{li,\, kj} &= \langle \varphi_l | F | \varphi_k \rangle\, \delta_{ik} - \langle \varphi_i | F | \varphi_j \rangle\, \delta_{kl} - (lk, ij) \\ B^{t}_{li,\, kj} &= -(lj, ik) \end{aligned}$$

These eigenvalues have a threefold degeneracy and the corresponding three eigenvectors are obtained from a unique eigenvector of E''^{t}, by using respectively $u^{t_2}_{li}$, $u^{t_2}_{li}$ and $u^{t_3}_{li}$: two of these variables are real and the third is purely imaginary.

For the wavefunctions themselves one then has:

with $u_{li}^{t_1}$: the orbitals with α and β spin values are no longer identical and the resulting wavefunction is an eigenfunction of S_z, but not of S^2.
with $u_{li}^{t_2}$ and $u_{li}^{t_3}$: the orbitals are no longer eigenfunctions of S_z, so the resulting wavefunction is neither an eigenfunction of S_z, nor of S^2.
with $u_{li}^{t_3}$: the orbitals and the resulting wavefunction are no longer real.

For the three possibilities the symmetry constraint may be retained or not according to whether φ_l and φ_i belong to the same symmetry representation or not.

2.3. *Instabilities of the Third Type ("non-real")*

The eigenvalues of E'' are obtained by diagonalizing the matrix:

$$E''^{c} = A^s - B^s = A^t - B^t \tag{8}$$

These eigenvalues have a fourfold degeneracy, and the eigenvectors are obtained by using the variables iu_s, iu_{t_1}, iu_{t_2} and iu_{t_3}. Three of them are purely imaginary and the fourth one is real.

The spin and symmetry properties of the orbitals are the same as in the first and second types, but here the variations of the orbitals are imaginary in the cases where they were real, and are real in the case where they were imaginary.

3. Results and Discussions

In the results presented in Table 1, one may notice a fair diversity in the examples of non-singlet instability, but only three "non-real" instabilities (MgO, O_2^{2-}, O_3) and only two singlet instabilities (O_2^{2-} and O_3).

3.1. *Singlet Instability*

3.1.1. Singlet Instability and Near Degeneracy Problem

For the sake of simplicity, let us first consider the diagonal matrix elements of E''^{s}. We see, from (6), that they look very much like excitation energies (it is the same for E''^{t} and E''^{c}). In fact one has

$$\begin{aligned} E''^{s}_{li,li} &= e_l - e_i + J_{li} + 3K_{li} \\ &= {}^1\Delta E_{li} + K_{li} \end{aligned} \tag{9}$$

${}^1\Delta E_{li}$ represents the excitation energy from the ground state to the singlet excited state resulting from an excitation in the φ_l orbital; e_l and e_i represent the energies of the orbitals φ_l and φ_i respectively; J_{li} and K_{li} are the Coulomb and exchange integrals.

Consequently, in this type of instability the existence of a degeneracy or a near degeneracy between Φ_{RHF} and another function is favourable for instability: these degeneracies may happen in the case of a long bond (because, when a bond is stretched, the energy of the Φ_{RHF} rises too much and crosses some excited states),

Table 1. Results of instability calculations

Molecule	Basis	Energy	Lowest eigenvalues of E''			Geometry	Symmetry	
			Singlet	Non-real	Non-singlet		Initial	After instability
F_2	GTO[c] double ζ	−198.7048	0.1966	0.1435	−0.1019	$d=2.68$ a.u.	$D_{\infty h}$	$C_{\infty v}$
MgO	STO[d] double ζ	−274.340	0.0362	−0.0022 −0.0022	−0.0529 −0.0529 −0.1876	$d=3.30$ a.u.	$C_{\infty v}$	none
O_2^{2-}	STO[b] double ζ $+(\zeta_{p_\pi}=0.3)$	−149.3086	−0.0025 −0.0025	−0.0187 −0.0187	−0.0083 −0.0083 −0.0247 −0.0381 −0.0381 −0.0588	$d=2.815$ a.u.	$D_{\infty h}$	none
N_2O_4	GTO[a] minimum	−406.3786	0.1398	0.1194	−0.0404 −0.1142 −0.1153	Ref. [1]	D_{2h}	C_s
Ethylene	GTO[a] minimum	− 77.6418	0.3482	0.2727	−0.0217	Ref. [2]	D_{2h}	C_{2v}
	GTO[e] double ζ	− 78.00118	0.3329	0.2659	−0.0112	Ref. [2]	D_{2h}	C_{2v}
	GTO[e] triple ζ	− 78.01334	0.3026	0.2425	−0.0115	Ref. [2]	D_{2h}	C_{2v}
Benzene	GTO[a] minimum	−229.701	0.2021	0.2423	−0.0418	Ref. [3]	D_{6h}	D_{3h}
Benzene Dewar	GTO minimum	−229.572	0.2627	0.2771	−0.0171 −0.0270	Ref. [4]	C_{2v}	none
Benzvalene	GTO minimum	−229.549	0.2682	0.2331	−0.0238	Ref. [5]	C_{2v}	none
Prismane	GTO minimum	−229.508	0.3294	0.3334	0.1462	Ref. [6]	D_{3h}	D_{3h}
Pentalene	GTO minimum	−304.995	0.0716	0.0268	−0.0927 −0.2392	[f]	D_{2h}	C_s

[a] Clementi, E.: Acta. Phys. **27**, 494 (1969).

[b] Clementi, E.: Table of atomic wavefunctions, supplement to paper: *Ab initio* computations in atoms and molecules, IBM Journal **9**, 2 (1965).

[c] Huzinga, S.: J. Chem. Phys. **42**, 1293 (1965).

[d] Basis a), increased from results of Yoshimine computations: J. Phys. Soc. Japan **25**, 1100 (1968).

[e] Basis c) from Huzinaga: contractions are given in Table 3.

[f] Pentalene computation was made in a D_{2h} geometry: C–C = 1.42 Å, C–N = 1.08 Å, CCC = 108°.

in the case of an excess of electrons, for instance in negative ions (because the highest energy levels are dense in this case), in the case of the π systems, and naturally also in some particular cases that are difficult to connect to a general rule.

The condition of degeneracy is particularly restrictive for the singlet type instability. The condition $E''^{s}_{li,li}<0$ means ${}^1\Delta E_{li}<-K_{li}$ and so there must exist one state below the RHF state separated from it by an energy larger than K_{li}. Such a situation is never realized in usual systems because ${}^1\Delta E_{li}>0$.

3.1.2. Singlet Instability and the Weight of Ionic Structures

It is possible to connect this property to the excessive weight of the ionic contribution in the usual Φ'^{s}_{RHF}. Let us consider a two-center system, (the centers being atoms or more generally fragments) and the atomic or hybrid orbitals χ_l (left hand side) and χ_r (right hand side) bonding the two centers. Suppose that χ_l and χ_r are equivalent and that their overlap can be neglected. Using the two following molecular orbitals

$$\varphi_i = \frac{1}{\sqrt{2}}(\chi_l + \chi_r) \qquad \varphi_k = \frac{1}{\sqrt{2}}(\chi_l - \chi_r) \tag{10}$$

one has for the RHF wave function:

$$\Phi_{\mathrm{RHF}} = (\mathrm{N}!)^{-1/2} |\ldots \varphi_i \, \overline{\varphi}_i \ldots|$$

Consider, now, singlet type variations of the wavefunction. The expression of the new wavefunction Φ' in terms of u_{ki}'s, limited to the second order is:

$$\Phi' = \{\psi + u_{ki}[|\ldots \varphi_k \, \overline{\varphi}_i \ldots| + |\ldots \varphi_i \, \overline{\varphi}_k \ldots|] + u_{ki}^2 |\ldots \varphi_k \, \overline{\varphi}_k \ldots|\} \left(1 - \frac{u_{ki}^2}{2}\right)$$

or, in terms of χ_l and χ_r:

$$\begin{aligned} \Phi' = \frac{1}{2} \Bigg\{ & |\ldots \chi_l \, \overline{\chi}_l \ldots| \left(1 - u_{ki}\sqrt{2} + \frac{u_{ki}^2}{2}\right) + |\ldots \chi_r \, \overline{\chi}_r \ldots| \left(1 + u_{ki}\sqrt{2} + \frac{u_{ki}^2}{2}\right) \\ & + \sqrt{2} \left[\frac{|\ldots \chi_l \, \overline{\chi}_r \ldots| + |\ldots \chi_r \, \overline{\chi}_l \ldots|}{\sqrt{2}} \right] \left(1 - \frac{u_{ki}^2}{2}\right) \Bigg\} \left(1 - \frac{u_{ki}^2}{2}\right) \end{aligned}$$

The weight of the covalent contribution to the wavefunction Φ' is equal to $(\frac{1}{2} - u_{ki}^2)$ instead of just $\frac{1}{2}$ in Φ_{RHF} and the weight of the total ionic contribution is equal to $(\frac{1}{2} + u_{ki}^2)$ in Φ' instead of $\frac{1}{2}$ in Φ. Furthermore, the left-right symmetry is broken since the coefficients of $|\ldots \chi_l \, \overline{\chi}_l \ldots|$ and $|\ldots \chi_r \, \overline{\chi}_r \ldots|$ are not equal. Probably, this increase of the ionic contribution is energetically unfavourable and it is not offset by the decreasing of the symmetry restriction (at least, in the systems we have studied).

3.1.3. Influence of the Off-Diagonal Terms

Let us consider now the influence of the off-diagonal terms of E''. If we argue in terms of localized orbitals (as Φ_{RHF} is invariant in any unitary transformation on the orbitals, so E'' and its eigenvalues are invariant), we have

$$E''^{s}_{i^*i,\, j^*j} \approx 4(i^*i, j^*j)$$

$$(i^*i, j^*j) = \int \varphi_{i^*}(1)\varphi_i(1)\varphi_{j^*}(2)\varphi_j(2) \frac{1}{r_{12}} \, d\tau_1 \, d\tau_2$$

where φ_i and φ_{j*} are respectively the bonding and anti-bonding orbitals of the same bond. But one has typically

$$(i^*i, j^*j)/{}^1\Delta E_{i^*i} \approx 0.1$$

and consequently, it is impossible for a single off-diagonal term to lead to a negative eigenvalue. For cyclic polyenes, it has been evaluated [11, 14] with semi-empirical calculations that a negative eigenvalue appears with a rather large (≈20) number of carbon atoms. At the *ab initio* level a similar situation is expected to appear when the number of the off-diagonal terms is large enough to counterbalance the fact that ${}^1\Delta E_{i^*i} = 0$ (in terms of localized orbitals) or equivalently when $e_{i^*} - e_i$ becomes small enough (in terms of canonical orbitals). However this situation has been met in neither of the cases studied here (cf. Sect. 3.1.6 below).

By these considerations, we attempt to explain the very small number of singlet instabilities we met. Let us try to explain the two instabilities (O_3 and O_2^{2-}) obtained in a full HF instability calculation (i.e. the matrix E''^s have been exactly diagonalized).

3.1.4.

For ozone, RHF wavefunctions have been calculated in a minimum GTO basis set, for three electronic configurations studied by Fischer-Hjalmars [22], whose global symmetry is ${}^1A_1$ (see Table 2). The molecule geometry was an isosceles triangle with the largest angle equal to 116° 49′ [23]. In Table 2, we see that the configuration III with the lowest energy does not show any singlet instability in conformity with the above analysis. On the other hand, the configurations I and II which are higher in energy do present a singlet instability. However, in the case of the configuration I, the eigenvector of E''^s corresponding to the negative eigenvalue is essentially built on the mixture of $2b_2$ and $4a_1$: the instability tends to change the configuration I into the configuration III, and the same holds for the configuration II. As the Φ_{RHF} associated to the configuration III is stable, an

Table 2. Instability calculations for ozone in various electronic configurations

Configurations	I $..1a_2^2, 4b_1^2, 2b_2^2$	II $..4b_1^2, 6a_1^2, 1a_2^2$	III $..1a_2^2, 6a_1^2, 2b_2^2$
$E_{\text{a.u.}}$	−223.385	−223.323	−223.508
λ_0^t	−0.0093 −0.1391 −0.2936	−0.0575 −0.1701 −0.3875	−0.0186 −0.2579
λ_0^c	−0.0045 −0.0993	−0.0049 −0.0632 −0.1327	0.0219
λ_0^s	−0.0621	−0.1004	0.0588

unrestricted Hartree-Fock calculation without symmetry restriction, but with spin restriction would probably lead to the same wavefunctions as in the RHF calculation. Such an instability may be coined "filling up instability": it is not connected with the existence of another wavefunction with lower symmetry and energy but only with another way of filling the symmetry orbitals.

However, the present calculation does not exclude that a UHF function having lower energy than the configuration III may exist.

3.1.5.

For O_2^{2-} several RHF calculations were made in an STO double-ζ basis enlarged by more and more diffuse functions for $2p_\pi$ and $2p_{\pi'}$ (correlatively, the energy decreases). The HF singlet instability appears with $\zeta_{2p}=0.3$. As the ζ_{2p} decreases, the two highest occupied orbitals (π_u and π_u') become more and more diffuse. Moreover, the instability direction corresponds to a transformation of the π_u orbital into a more diffuse orbital and a transformation of the π_u' orbital into a more concentrated orbital: these transformations lead to a loss of a cylindrical symmetry. This result may be explained by assuming that the energy of a configuration $|\ldots \pi_g^2\, \pi_u'^2\, \pi_u^2 \ldots|$ of O_2 is lower than the energy of the present configuration of O_2^{2-}: in our calculation of O_2^{2-}, two electrons tend to fly away from the molecule, in the limits that are allowed by our LCAO basis (in a complete basis set these electrons would be completely ejected). This explanation must be regarded only as a conjecture but, it is consistent with the calculation of Delgado and Prat [17] on the atomic ion O^{2-}.

3.1.6. The Polyenes

In our results, no evidence of singlet instability appears for polyenes but it should be noted that in semiempirical theories there is a singlet instability only for systems with more than 20 π electrons and we have not tried to compute such large systems. In fact, the value that we find for the lowest eigenvalue λ_0^s of E''^s decreases when the size of the system increases (ethylene, benzene, pentalene) but it cannot be concluded from this behaviour that λ_0^s becomes actually negative for larger systems, although it is generally concluded that it must be so on the basis of general considerations on the orbital spacing and on the behaviour of the integrals.

In the case of pentalene, semiempirical calculations with optimization of the geometry [24, 25] indicate that the alternant conformation has a lower energy than the D_{2h} conformation. In spite of this we have found here no trace of singlet instability in the D_{2h} geometry. Similarly no singlet instability is found in semiempirical calculation with D_{2h} geometry when spectroscopic parameters are used. It may well be that the RHF function with D_{2h} symmetry does not correspond to the absolute HF minimum in D_{2h} geometry.

3.2. *Non-Singlet (or Triplet) Instability*

3.2.1. General Discussion

The large diversity of non-singlet instability in our results, may be correlated with the following properties:

1) A calculation similar to the one we made for the singlet instability shows a decreasing of the ionic contribution in the case of the non-singlet instability: for the system described by the MO's of the form (10), this contribution is changed from $\frac{1}{2}$ (in Φ_{RHF}), to $\frac{1}{2}-u^2$ in the transformed wavefunction Φ' for each of the three variables, u_{t_1} and u_{t_2} (real) and u_{t_3} (purely imaginary).

2) The relative abundance of non-singlet instabilities can be understood by considering the diagonal terms of the matrix E''' of the Eq. (7), we have:

$$E'''_{li,li}=e_l-e_i-J_{li}-K_{li}={}^3\Delta E_{il}-K_{li} \tag{11}$$

As in the singlet case, a degeneracy or a near degeneracy in the SCF levels is favourable to instability. In the present case, however, the condition:

$$e_l-e_i-J_{li}<0 \tag{12}$$

is sufficient (in the singlet case, it is necessary but not sufficient) and in fact, it is even not necessary, for it is possible to obtain an instability with

$$e_l-e_i-J_{li}>0$$

assuming that this quantity has a small positive value (smaller than K_{li}).

This particular situation is well illustrated by the study of the dissociation of H_2. It is well known that the RHF behaviour is not correct as concerns its radicalic dissociation, because the ionic contribution still has the value of 1/2 even when the two atoms are completely separated, but that this contribution tends to zero in a SCF calculation without constraints. We have seen that the Φ_{RHF} of this system never shows singlet instability. In addition, as shown in Fig. 1 non-singlet instability appears for $R>R_I=2.3$ a.u. For large separations, the SCF triplet is lower in energy than Φ_{RHF}, but for middle separations the same triplet is above the Φ_{RHF} function, and there is still a non-singlet instability; for separations near the equilibrium distance (1.43 a.u.), the triplet state is too high and there is no more instability. In most of the examples of non-singlet instability studied here, the lowest triplet state is above the calculated RHF state (except MgO and O_3).

3.2.2. Diradicals

The fact that non-singlet instability is obtained even when the triplet state is above the Φ_{RHF} shows that it is not possible to establish an unambiguous relation between the existence of non-singlet instability and the biradical structure of a system.

However, the systematic study of the nature of the reactional intermediary assumed by Fukutome [26] and Yamaguchi and Fueno [27, 28] illustrates the fact that the crossing of MO energy levels along the reaction path proves very probably the

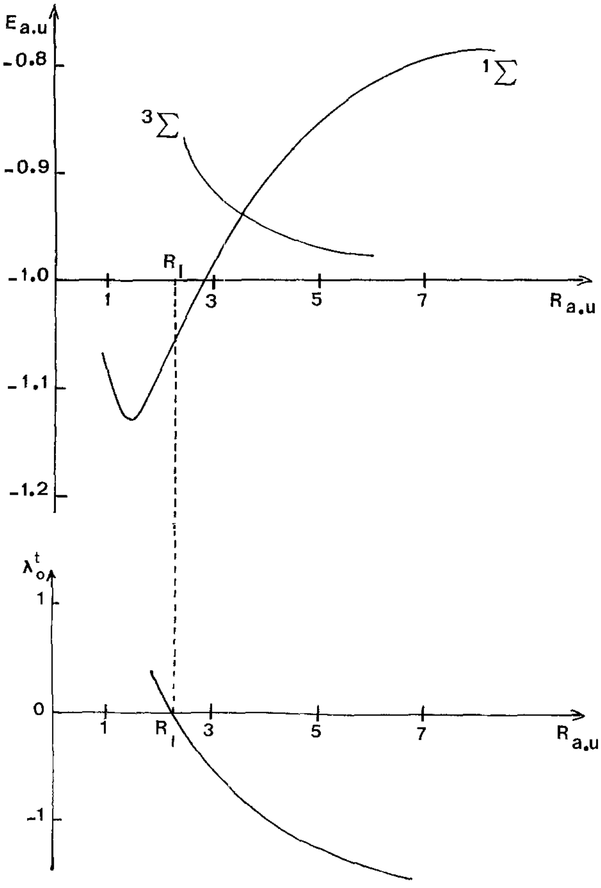


Fig. 1. Energy of H_2 molecule versus interatomic distance, in an uncontracted 6*s*-GTO basis; and lowest eigenvalue of E'''^t versus the interatomic distance

existence of a biradical intermediary. In another connection, a crossing of MO energy levels implies non-singlet instability. So, we have here a typical case where biradical character and non-singlet instability are simultaneously present, without any implication relation between both properties. In fact, level crossing is a more restrictive condition than non-singlet instability.

3.2.3. The case of σ Systems

As far as usual molecules are concerned, (and not reaction intermediaries) the triplet state is generally too high and the exchange integral K too small in the σ systems. For example in C–C or C–H bonds, we have

$$^3\Delta E_{li} \approx 1 \text{ a.u.} \qquad K_{li} \approx 0.5 \text{ a.u.}$$

and consequently, non-singlet instabilities in a system of hydrocarbons may only be expected in large molecules (as singlet instability in polyenes). This problem does not seem to have been studied so far.

We found only three non-singlet instabilities in the σ systems of the following compounds: N_2O_4, F_2 and MgO. The molecule N_2O_4 was selected because of the particular electronic structure with an abnormally long N–N bond [31–33]. The two other cases, F_2 and MgO, have to be connected with the non-existence of a binding energy at the SCF level. For F_2, a UHF calculation was made, in order to compare it with a CI: the decrease in energy ΔE_{UHF} is sevenfold smaller than the ΔE_{CI} obtained with a CI involving the same orbitals,

$$\Delta E_{\mathrm{UHF}} = -0.010 \text{ a.u.}$$
$$\Delta E_{\mathrm{CI}} = -0.073 \text{ a.u.}$$

and so it would be quite illusive to hope that a UHF calculation can serve as substitute for CI (note that neither the UHF nor CI calculation performed here predict the correct sign of the dissociation energy).

3.2.4. The Case of the π Systems

If now π systems are considered, triplet states are low and simultaneously the corresponding exchange integrals are particularly large (this is to be connected with a larger correlation energy in π systems than in σ systems). Correlatively, non-singlet instability in the π system is found in all the studied examples: ethylene, benzene, Dewar benzene, benzvalene, pentalene, N_2O_4, O_3 and O_2^{2-}. These results are in perfect agreement with the results of semiempirical calculations of Paldus and Čižek [12–15], Fukutome [8], Koutecký [11], etc. So, it seems that non-singlet instability exists in any π system, even in non-conjugated ones. In ethylene, the instability direction corresponds to the vanishing of the left-right symmetry, and consequently the two fragments $-CH_2$ are no longer equivalent; yet the σ-π distinction is preserved, at least at this stage of the calculation (of course, we cannot deduce from the present study what would happen if a true UHF minimization was achieved).

In more complicated π systems, the instability direction corresponds to the mixture of bonding and antibonding π orbitals of the whole π system, and with the same reservations as in ethylene, the σ-π distinction is preserved.

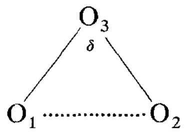
Moreover, it seems, from calculations on the allyl radical [18, 19], that the size and the particular choice of the AO basis are very important in this problem. As all the above calculations were made in a minimum basis set, we tried other basis sets, on the example of ethylene. We performed calculations in the double and tri-ζ GTO basis presented in Table 3. As shown in Table 1, the total energy of the molecule decreases with the increasing of the basis size, but there is always a non-singlet instability.

Other examples of non-singlet instabilities in π-systems are given in inorganic systems: O_3, O_2^{2-}.

Table 3. Contractions for extended basis set of Gaussian functions used in the calculations of ethylene

Gaussian exponents			Double-zeta contraction	Triple-zeta contraction
C	*S*	4232.61	0.002336	0.002336
		634.882	0.017884	0.017884
		146.097	0.086818	0.086818
		42.4974	0.298521	0.298521
		14.1892	0.686791	0.686791
		5.14773	0.772924	1.0
		1.96655	0.257253	1.0
		0.496240	1.0	1.0
		0.153310	1.0	1.0
	P	18.1557	0.0391963	0.0391963
		3.98640	0.244143	0.244143
		1.14293	0.816773	0.816773
		0.359450	0.668140	1.0
		0.114600	0.417933	1.0
H	*S*	13.3615	0.032828	0.032828
		2.01330	0.231208	0.231208
		0.453757	0.817238	1.0
		0.123317	1.0	1.0

In ozone, non-singlet instabilities exist in every configuration we calculated. As far as the lowest configuration is concerned, the following remarks can be made:



$\delta = 116°\ 49'$

1) The bonding and antibonding σ orbitals, respectively in symmetry representation a_1 and b_1, are both occupied and consequently there is no "σ-bond" between the atoms O_1 and O_2 at the RHF stage.

2) In the π-system, one orbital of symmetry a_2 antibonding between O_1 and O_2 is occupied, and the instability direction corresponds to the mixture of this orbital a_2 with a virtual π orbital of symmetry b_2, bonding between O_1 and O_2.

This means that the instability tends to transform Φ_{RHF} into a wavefunction corresponding to the general biradical description of ozone [30]: however, it should not be concluded that ozone could have a paramagnetic structure.

The instability direction for O_2^{2-} corresponds, as for the singlet case, to a loss of the cylindrical symmetry according to the following mixtures:

Singlet instability case:

$$\pi_u \longrightarrow (\pi_u + \lambda\pi_u^*)$$
$$\pi_u' \longrightarrow (\pi_u' - \lambda\pi_u'^*)$$

Non-singlet instability case:

$$\pi_u \longrightarrow (\pi_u + \lambda' \overline{\pi}_u^*)$$
$$\pi'_u \longrightarrow (\pi'_u - \lambda' \overline{\pi}_u'^*)$$

In the singlet case the above mixing leads 1) to an orbital which is more diffuse than π_u and 2) to an orbital which is more concentrated than π'_u. But the effect of the mixture cannot be described in such simple terms in the non-singlet case because the concerned MO's have different spin function. And so the non-singlet instability of O_2^2 cannot be related to an ionization as simply as in O^{2-} [17].

3.3. *Instability of the Third Type*

The "non-real" instability is an intermediate case between singlet and non-singlet instabilities: this can be seen by considering the ionic contribution weight (the ionic contribution is equal to 0.5 for each Φ' functions as for Φ_{RHF} (cf. Sect. 3.1.2.) corresponding to the four u variables concerned here) as well as by considering the diagonal matrix elements of E''^c:

$$E''^c_{ki,ki} = e_k - e_i - J_{ik} + K_{ik}$$

From this last expression, we can deduce that singlet instability implies non-real instability, that itself implies non-singlet instability, (with the reservation that the off-diagonal terms influence in the same way the results for the three cases).

It may seem surprising that non-real instability is more difficult to obtain than non-singlet instability, since *a priori* a supplementary restriction – the real nature of the MO's – is dropped. However, we may notice that one of the variables u^t_{li} associated with the so called non-singlet instability, is purely imaginary, and that one of the variables u^c_{li} associated with the so-called non-real instability, is real. Furthermore, the MO variations are either real, or purely imaginary and the former type of variation is not more particular than the latter.

We obtained non-real instabilities with O_3, O_2^{2-} and MgO. In the latter case, the instabilities are gathered in Table 4 where the diagonal terms of E''^s, E''^t and E''^c are given. We see that the influence of the off-diagonal term is smaller than 0.07 a.u. Moreover, for the two mixtures illustrated in Table 4, the terms $(\Delta E - J)$ are very small: as $K_{2\pi, 7\sigma}$ is very small too, the difference between the corresponding diagonal elements of E''^c and E''^t are not important and instabilities of these two

Table 4. Diagonal terms of E'' matrix for different types of instability in MgO: the values in italics correspond to the cases where a negative eigenvalue of E'' is found

Mixture of orbitals involved by instability	E''_t Non-singlet	E''_c Non-real	E''_s Singlet
$6\sigma \rightarrow 7\sigma$	*−0.14*	0.10	0.33
$2\pi \rightarrow 7\sigma$	*0.03*	*0.05*	0.07

types are obtained; this fact does not occur for the mixture 6σ-7σ because the corresponding $K_{6\sigma,7\sigma}$ is bigger.

Furthermore the starting direction of instability can suggest that the (2π-7σ) diexcitation is an important component of a configuration interaction, while the actual CI calculation, performed by Huron and Rancurel [29] shows that it is negligible compared with the contribution of the (6σ-7σ) diexcitation.

4. Conclusion

Our results show the existence of Hartree-Fock instabilities in *ab initio* calculations for molecular systems of small and medium size, and so lead to a generalization of previous semiempirical [10–15] and *ab initio* results [16, 17].

In the present calculations, no evident correlation has been found between instability and physical properties of the molecule in contrast with the correlation found in the case of polyenes.

Furthermore, most of the instabilities that we have found belong to the non-singlet type. Indeed singlet instability can occur only if an increasing weight of the ionic contribution in the wavefunction has a favourable effect on the energy or if it is balanced by other factors (symmetry . . .). On the contrary the weight of the ionic contribution decreases in non-singlet type variations.

The main cause of instability at the RHF level is a degeneracy or a near degeneracy of the energy of Φ_{RHF} with another configuration, or an inversion of states, or a large electronic repulsion: this occurs in π systems and in negative ions, and in some less foreseeable cases as MgO and F_2 (it is to be noticed that in these last two cases Φ_{RHF} provides a negative bond energy and Φ_{UHF} too, so that a UHF calculation cannot be used as substitute for a CI). The inversion of states essentially appears in the "filling up instabilities" in which the UHF function is not more general than the initial RHF function, but is constructed with different set of occupation numbers for the various symmetries.

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