The Validity of the Hartree-Fock (HF) Picture in Diamagnetic Binuclear Transition Metal Compounds: trans$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$

Michael C. Böhm
Institut für Organische Chemie der Universität Heidelberg, West Germany

Z. Naturforsch. **37a**, 241—247 (1982); received February 4, 1982

The Thouless instability conditions in the binuclear iron complex **1** have been investigated by means of a semiempirical INDO approach. The behaviour of the restricted Hartree-Fock (HF) wave function with respect to singlet, non-singlet and complex variations of the orbitals is studied. The existence of a spin decoupled solution near the diamagnetic closed shell groundstate is demonstrated. The nature of the correlation processes (angular vs left-right) for the various orbital fluctuations is discussed.

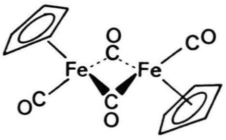
Introduction

The electronic structure of binuclear transition metal compounds with a diamagnetic groundstate has been investigated in large detail in recent years [1]. From a theoretical point of view two aspects were of main interest. On one side the magnitude of the direct metal-metal interaction in bridged systems has been studied extensively [2—5].

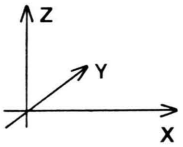
On the other side the general validity of the one-determinantal Hartree-Fock (HF) picture has been questioned as CI calculations on several binuclear species have demonstrated the significant importance of electron correlation [6, 7].

Recently we have shown that the two theoretical problems (magnitude of direct metal-metal interaction vs coupling via ligand bridges and the validity of the one-electron picture within the HF approximation) can be unified by means of theoretical procedures investigating the stability of the HF wave function against orbital fluctuations [8—11]. The formalism is based on the random phase approximation (RPA) and has been derived by Thouless [12]; Čiček and Paldus have reformulated the eigenvalue problem for the excitation energies of a N electron system for quantum-chemical purposes [13]. In the field of transition metal complexes the method has been applied to poly-decker sandwiches [8, 9] bimetallocenes and bimetallocenylenes [10] as well as to binuclear cyclooctatetraene complexes [11].

In this publication we want to investigate the stability of the HF solution, the nature and the range of electron correlation and the participation of the bridging ligands in many body effects in the iron complex trans$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (**1**). Theoretical framework of this study are the instability conditions as derived by Thouless [12]; computational framework is an improved INDO Hamiltonian designed for transition metal compounds [14].



1



Theory

Based on RPA the stability of the HF orbitals against the following variations is investigated:

a) Violation of the spatial symmetry while the orbitals are spin-paired (α and β spin) and retain their real character.

b) Violations of the spatial and spin symmetry leading to an unrestricted solution of the HF determinant.

c) Violation of the real character of the orbital wave function leading to complex solutions for the one-electron functions.

The stability condition of the HF determinant $|\Phi_0\rangle$ can be formulated as an eigenvalue problem for the excitation energies ${}^{1,3}\lambda$ for the N electron

---

Reprint requests to Dr. M. C. Böhm, Institut für Organische Chemie der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg.

0340-4811 / 82 / 0300-0241 $ 01.30/0. — Please order a reprint rather than making your own copy.

system [13, 15, 16].

$$\begin{pmatrix} {}^{1,3}X & {}^{1,3}Y \\ {}^{1,3}\bar{Y} & {}^{1,3}\bar{X} \end{pmatrix} \begin{pmatrix} {}^{1,3}C \\ {}^{1,3}\bar{C} \end{pmatrix} = {}^{1,3}\lambda \begin{pmatrix} {}^{1,3}C \\ {}^{1,3}\bar{C} \end{pmatrix}. \tag{1}$$

${}^{1,3}X$ symbolizes the matrix with singly excited configurations on the diagonal and the mutual interaction energies on the off-diagonal; ${}^{1,3}Y$ stands for the CI matrix between doubly excited configurations and the HF groundstate, C is the column matrix of mixing amplitudes between the occupied and empty Fermi-sea, ${}^{1,3}\bar{X}$, ${}^{1,3}\bar{Y}$ and $\bar{C}$ are the complex conjugates of ${}^{1,3}X$, ${}^{1,3}Y$ and C. The matrix elements of ${}^{1,3}X$ and ${}^{1,3}Y$ are defined in eq. (2) and (3); the upper signs correspond to orbital fluctuations of the singlet type (${}^{1}X$, ${}^{1}Y \rightarrow {}^{1}\lambda$), the lower ones are associated to triplet (non-singlet) excitations (${}^{3}X$, ${}^{3}Y \rightarrow {}^{3}\lambda$).

$$\begin{aligned} {}^{1,3}X_{kl,jm} &= (\varepsilon_l - \varepsilon_k)\,\delta_{kj}\,\delta_{lm} + (k\,l, j\,m) \\ &\quad - (k\,j, l\,m) \pm (k\,l, j\,m) \end{aligned} \tag{2}$$

$$\begin{aligned} {}^{1,3}Y_{kl,jm} &= (k\,l, j\,m) - (k\,m, j\,l) \\ &\quad \pm (k\,l, j\,m) \end{aligned} \tag{3}$$

The indices k and j correspond to orbitals occupied in the HF groundstate $|\Phi_0\rangle$, l and m refer to the particle-states. The orbitals φ_k have been obtained by means of the real, restricted HF eigenvalue problem (4) where F symbolizes the Fock operator.

$$F\,|\varphi_k\rangle = \varepsilon_k\,|\varphi_k\rangle\,. \tag{4}$$

The electron-electron interaction integrals in (2) and (3) are defined in eq. (5):

$$(k\,l, j\,m) = \left\langle \varphi_k(1)\,\varphi_l(1) \left| \frac{1}{r_{12}} \right| \varphi_j(2)\,\varphi_m(2) \right\rangle. \tag{5}$$

The excitation energies ${}^{1,3}\lambda$ are positive if the interaction matrix on the left of Eq. (1) is positive definite. According to Thouless this condition also guarantees the stability of $|\Phi_0\rangle$ against orbital fluctuations.

If the spin-orbitals $|\varphi_k\rangle_\sigma$ are associated to $|\Phi_0\rangle$, the orbitals of the determinantal wave function $|\Phi\rangle$ resulting from the eigenvalue problem (1) are given by the expansion (6) where the spin-orbitals $|\varphi_k\rangle_\sigma$ have been replaced by one-electron functions $|\varphi_k\rangle'_\sigma$ with mixing amplitudes $c_{k\sigma l\sigma'}$.

$$|\varphi_k\rangle'_\sigma = |\varphi_k\rangle_\sigma + \sum_{l=N+1}^{\infty} c_{k\sigma l\sigma'}\,|\varphi_l\rangle_{\sigma'}\,. \tag{6}$$

$$|\varphi_k\rangle_\sigma = |\varphi_k\rangle\,|\sigma(s)\rangle\,, \quad s = {}^{\alpha}_{\beta}\ \text{spin}\,. \tag{7}$$

The unitary transformations (8)—(11) form a proper one-electron basis for the singlet (${}^{1}\lambda$) and triplet (non-singlet (${}^{3}\lambda$)) excitations.

$$c^{s}_{kl} = (1/\sqrt{2})\,(c_{k\alpha l\alpha} + c_{k\beta l\beta})\,, \tag{8}$$

$$c^{t}_{kl} = (1/\sqrt{2})\,(c_{k\alpha l\alpha} - c_{k\beta l\beta})\,, \tag{9}$$

$$c^{t'}_{kl} = (1/\sqrt{2})\,(c_{k\beta l\alpha} + c_{k\alpha l\beta})\,, \tag{10}$$

$$c^{t''}_{kl} = (1/\sqrt{2})\,(c_{k\beta l\alpha} - c_{k\alpha l\beta})\,. \tag{11}$$

Obviously (8) is associated to the singlet excitation while (9)—(11) correspond to the UHF problem.

In the case of a complex MO basis the four amplitudes $i c^{s}_{kl}$, $i c^{t}_{kl}$, $i c^{t'}_{kl}$ and $i c^{t''}_{kl}$ result in a single eigenvalue problem (12) which is fourfold degenerate due to the identity (13).

$$({}^{1}X - {}^{1}Y)\,C^{c} = {}^{c}\lambda\,C^{c}\,, \tag{12}$$

$${}^{1}X - {}^{1}Y = {}^{3}X - {}^{3}Y\,. \tag{13}$$

The singlet and triplet fluctuations are calculated by means of the interaction matrices (${}^{1}X + {}^{1}Y$) and (${}^{3}X + {}^{3}Y$), respectively, which together with the choice ${}^{1,3}X - {}^{1,3}Y$ for the complex amplitudes result in an eigenvector spectrum which is identical to the eigenvector set of (1).

HF solutions are called singlet stable if ${}^{1}\lambda > 0$; here only spatial violations of the orbitals are taken into account. The non-singlet (triplet) stability is related to ${}^{3}\lambda > 0$, the associated eigenvalue problem corresponds to spatial and spin violations of the HF orbitals. The stability of the HF orbitals against complex (non-real) variations is determined by ${}^{c}\lambda > 0$. The global stability of $|\Phi_0\rangle$ therefore can be expressed as $\min({}^{1}\lambda, {}^{3}\lambda, {}^{c}\lambda) > 0$.

In [8] and [10] we have discussed in large detail the occurance of the three instability types in binuclear transition metal compounds. The theoretical findings can be summarized as follows.

a) Singlet instabilities are the result of intraatomic angular correlation [17] and interatomic left-right correlation [17]. Only if both correlation processes are present in an orbital fluctuation, singlet instabilities are observed. The necessity of coupling both many body interactions results in correlation processes strongly dependent on the topology of the surrounding ligand system (e.g. different many body interactions in poly-decker sandwiches and bimetallocenes/bimetallocenylenes [8, 10]). In the stacked sandwich compounds high-lying valence orbitals of the central ring belonging to different irreducible representations allow the coupling of both correlation types (angular, left-right) resulting in significant singlet instabilities. In the bimetallocenes/bimetallocenylenes on the other side the combination of both processes is prevented due to the fulvalene bridge with a single high-lying fragment orbital of π-type. The interatomic left-right correlation prevents the intraatomic angular scattering which corresponds to an orbital transition within an electron-hole pair with large metal 3d amplitudes of different magnetic quantum numbers. The fluctuation pattern of the angular process on the other hand prevents left-right correlation. A schematical representation of this situation is displayed in Figure 1. An additional condition for singlet instabilities consists in the interaction with a nearby fluctuation showing similar many body dynamics via the off-diagonal elements of the instability matrix.

b) Triplet (non-singlet) instabilities correspond to a spin decoupling within an electron-hole pair with the same magnetic quantum number but with different parity with respect to the internuclear 3d3d axis (long-range behaviour, left-right correlation). Schematically the orbital fluctuations leading to the two instability types can be formulated by means of (15), (16) and (17).

Singlet instability:

$$(3\,\mathrm{d}_x)_\mathrm{i} \rightarrow (3\,\mathrm{d}_y)_\mathrm{o} \tag{15}$$

coupled to

$$(3\,\mathrm{d}_y)_\mathrm{o} \rightarrow (3\,\mathrm{d}_x)_\mathrm{i}\,. \tag{16}$$

Triplet instability:

$$(3\,\mathrm{d}_x)_\mathrm{i} \rightarrow (3\,\mathrm{d}_x)_\mathrm{o}\,, \tag{17}$$

$$x, y = z^2, xz, yz, x^2 - y^2, xy\,, \tag{18}$$

$$x \neq y\,. \tag{19}$$

For sake of clearness only the 3d contribution to the orbital wave functions is displayed. x and y symbolize a member of the 3d AO's while i and o stand for the parity of the orbital wave function (i = in-phase, bonding linear combination, o = out-of-phase, antibonding linear combination).

The INDO Hamiltonian used in the present instability calculation has been described in great

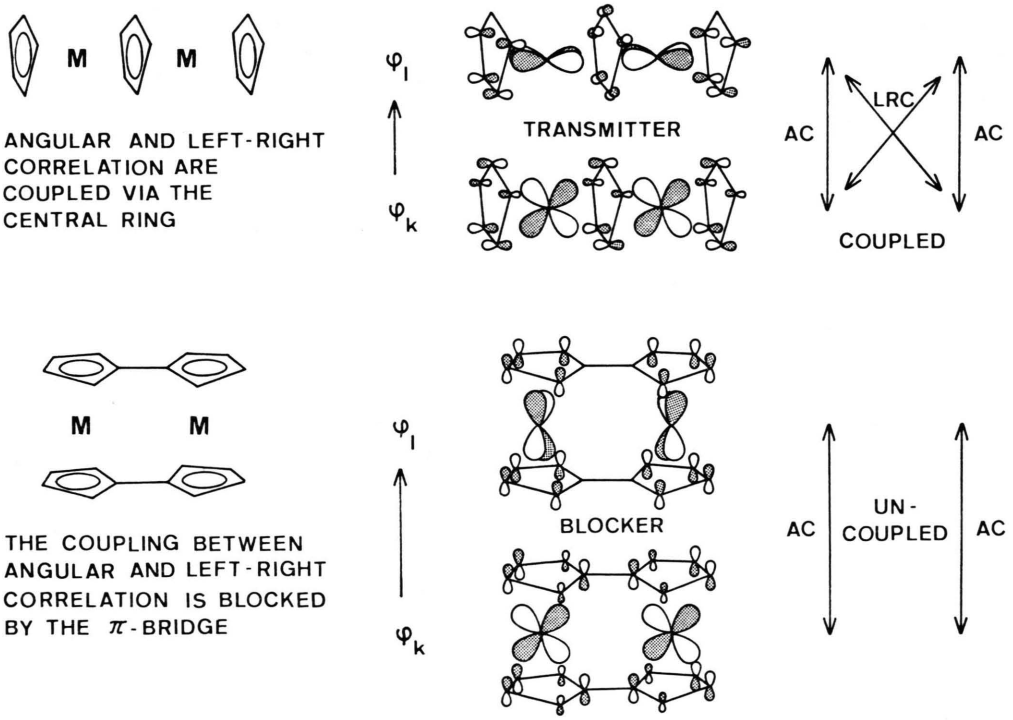


Fig. 1. Schematic representation of the coupling of intraatomic angular and interatomic left-right correlation in polydecker sandwich compounds. In bimetallocenes and bimetallocenylenes the angular correlation is decoupled from the left-right interaction and corresponds to a localized molecular domain (verified in the case of a bimetallocenylene complex).

detail in [14]; here only a short review of the parametrization scheme is given. H_{INDO} is defined in (20) by means of creation and destruction operators $a^{+}_{\mu\sigma}$ and $a_{\mu\sigma}$ associated to the μ'th AO with spin $\sigma(\sigma = \alpha, \beta)$.

$$\begin{aligned} H_{\mathrm{INDO}} = {} & \sum_{\mu}^{\mathrm{A}} \sum_{\sigma} U_{\mu\mu} n_{\mu\sigma} + \sum_{\mu}^{\mathrm{A}} \sum_{\sigma} \sum_{\mathrm{B} \neq \mathrm{A}} V^{\mathrm{AB}}_{\mu\mathrm{B}} n_{\mu\sigma} + \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \sum_{\sigma} \beta^{\mathrm{AB}}_{\mu\nu} a^{+}_{\mu\sigma} a_{\mu\sigma} \\ & + \tfrac{1}{2} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{A}} \sum_{\sigma} \sum_{\sigma'} (\gamma^{\mathrm{AA}}_{\mu\nu} - \tfrac{1}{2} K^{\mathrm{AA}}_{\mu\nu})\, n_{\mu\sigma} n_{\nu\sigma'} + \tfrac{1}{2} \sum_{\substack{\mu \\ \mathrm{A} \neq \mathrm{B}}}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \sum_{\sigma} \sum_{\sigma'} \gamma^{\mathrm{AB}}_{\mu\nu} n_{\mu\sigma} n_{\mu\sigma'} \,. \end{aligned} \tag{20}$$

$n_{\mu\sigma}$ is the number operator which is defined in (21).

$$n_{\mu\sigma} = a^{+}_{\mu\sigma} a_{\mu\sigma} \,. \tag{21}$$

The $U_{\mu\mu}$ parameters are atomic core integrals, the expectation value of an electron μ at the A'th atomic side in its own potential field and the field of the atomic core A. Experimental $U_{\mu\mu}$ values have been used. $V^{\mathrm{AB}}_{\mu\mathrm{B}}$ symbolizes the electron core interaction between the AO μ at center A and the atomic cores B (B $\neq$ A). $\beta^{\mathrm{AB}}_{\mu\nu}$ is the resonance integral between the atomic orbitals μ and ν at the centers A and B. $\beta^{\mathrm{AB}}_{\mu\nu}$ has been designed to be proportional to the interference density which is the physically significant term leading to bond formation (see [14]). The following two expressions are the one-center electron-electron interaction integrals of Coulomb ($\gamma^{\mathrm{AA}}_{\mu\nu}$) and exchange ($K^{\mathrm{AA}}_{\mu\nu}$) type which have been obtained from atomspectroscopic data. In the case of the $K^{\mathrm{AA}}_{\mu\nu}$ integrals a rotationally invariant ansatz has been used. The two-center Coulomb integrals $\gamma^{\mathrm{AB}}_{\mu\nu}$ are calculated via the empirical Dewar-Sabelli, Ohno-Klopman relation (22) [18].

$$\gamma^{\mathrm{AB}}_{\mu\nu} = 1 \,|\, \sqrt{R^2_{\mathrm{AB}} + 0.25(1 \,|\, \gamma^{\mathrm{AA}}_{\mu\mu} + 1 \,|\, \gamma^{\mathrm{BB}}_{\nu\nu})^2} \,. \tag{22}$$

R_{AB} is the separation between the atoms A and B.

The instability threshold as well as the absolute values of the excitation energies obviously depend on the parameters of the semiempirical Hamiltonian. Detailed studies in HF instability calculations within semiempirical MO procedures and ab initio approaches however have demonstrated that the general features concerning the stability of the HF solution are independent of the computational procedure [19, 20].

In the present paper the interrelation between short-range and long-range correlation effects as well as the role of the bridging groups with respect to the aforementioned many body interactions are studied. In accordance with [19] and [20] the general conclusions should be independent from the used MO model. This work differs from the aims of a recent ab initio HF instability study on quadrupoly bonded Cr and Mo complexes [21] as in the present investigation the important influence of bridging ligands in weakly coupled dimers upon electron correlation is analyzed but not the nature of the metal-metal bond.

The INDO HF and instability calculations on the binuclear Fe complex **1** with idealized C_{2h} symmetry were performed on the geometry determined by X-ray investigations [4, 22].

Calculations

The electronic structure of **1** has been discussed on several degrees of sophistication ranging from Extended Hückel (EH) calculations of the one-electron type [3], semiempirical CNDO results [5] to ab initio calculations with a near minimal basis [3]. The valence orbitals of **1** can be obtained from the fragment MO's of trans[(η^5-C_5H_5)Fe]$_2$ and the donor and acceptor functions of the carbonyl ligands. The FeCp dimer is an isolabal derivative [23] to $Fe_2(CO)_6$ extensively discussed by Thorn and Hoffmann [24]. In Fig. 2 the valence orbitals of **1** are displayed; they have been observed from the valence set of trans[(η^5-C_5H_5)Fe(CO)]$_2$ and from the two bridging carbonyl groups.

The orbital energies of **1** correspond to the semiempirical INDO Hamiltonian. The HOMO ($14b_g$) shows significant metal-metal coupling of π^* type ($3d_{xy}$) stabilized by the b_g combination of the CO acceptors. $14b_g$ is separated by about 1.9 eV from two orbitals, $31a_g$ and $16a_u$, with FeFe σ coupling and FeFe π interaction. The corresponding destabilized combinations are predicted at -1.27 and 0.60 eV. The lowest unoccupied MO ($29b_u$) however is of σ^* type (FeFe interaction) stabilized by the b_u combination of the π^*(CO) set. These occupied and virtual orbitals have large amplitudes in the FeFe direction. At lower energy a set of six MO's with large 3d contributions is predicted which are predominantly involved in the Fe-(C_5H_5) and

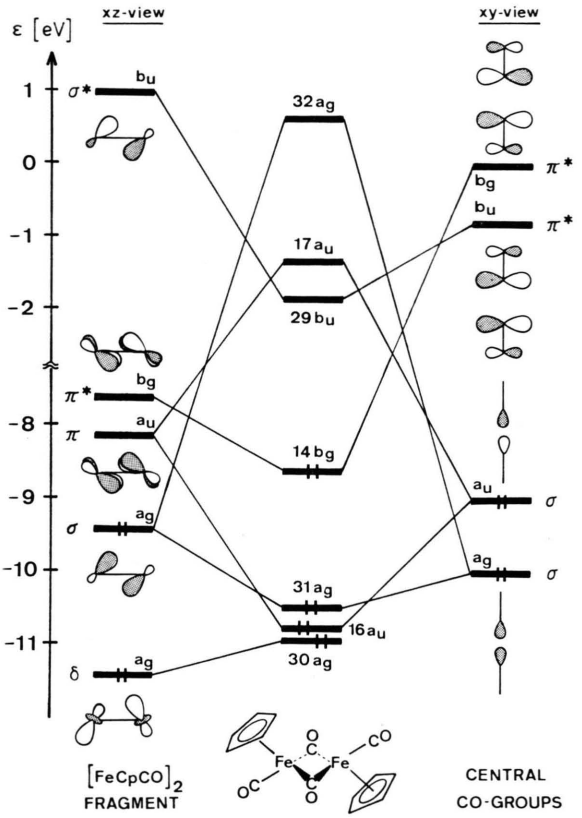


Fig. 2. Schematical interaction diagram for **1**. The valence orbitals of the binuclear complex are constructed from the fragment MO's of trans [(η^5-C_5H_5)Fe(CO)]$_2$ and from those of the bridging carbonly groups.

Fe(CO)$_{\text{terminal}}$ bonding. The highest MO ($30a_g$) of this Fe 3d set is of δ type and is predicted at -10.87 eV. The INDO results are close to the orbital splitting obtained within the ab initio framework [3].

The results of the HF instability calculations are summarized in Table 1. It is seen that the HF determinant $|\Phi_0\rangle$ is clearly stable with respect to orbital fluctuations of the singlet and complex (nonreal) type. The lowest root of the two eigenvalue problems exceeds 1 eV indicating the stability of the HF determinant against spatial violations and complex MO solutions. The leading term in the orbital fluctuations of $^1\lambda$ for the singlet instability corresponds to the excitation $14b_g \rightarrow 29b_u$. The associated correlation process at the Fe centers is of intraatomic angular type ($3d\pi^* \rightarrow 3d\sigma^*$). The symmetry of the valence orbitals at the bridging CO groups prevents left-right correlation and thus a further reduction of the excitation energy of the singlet instability problem.

The second eigenvalue of the singlet variation which is nearly degenerate with λ_1 corresponds to an angular correlation ($3d\delta \rightarrow 3d\sigma^*$) with a superimposed left-right coupling. The significant energy gap within the electron-hole pair however avoids the occurance of a HF breakdown of the singlet type. The λ_i values and the excitation patterns of the complex route are close to the singlet case.

The INDO results of the non-singlet variations differ remarkably from the HF fluctuations retaining the spin-paired character of the groundstate determinant. The lowest eigenvalue (0.15 eV) indicates the existence of an unrestricted HF solution that differs only 14.5 kJ/mol from the restricted HF wave function with a diamagnetic closed shell structure. Inspection of Table 1 clearly displays that the orbital transition corresponds to a spin decoupling within an electron-hole pair of π^* and π character (FeFe coupling). The (approximate) magnetic quantum number in both MO's is identical, the parity of the orbital wave function with respect to the internuclear FeFe axis however differs. This MO pattern results in a spin decoupling between the two formal (η^5-C_5H_5)Fe(CO)$_2$ fragments. In contrast to the singlet fluctuations this process is always of interatomic long-range character. More pronounced non-singlet fluctuations in **1** are prevented due to the significant delocalization of the orbital wave function of the $14b_g$ hole-state.

In the case of observed non-singlet instabilities it is clear that the predictive capability of HF calculations concerning the spin multiplicity of polynuclear clusters (e.g. closed shell complex with low-spin configuration vs. open shell system with high-spin configuration) is lost. Here methods beyond the independent particle picture must be employed. Possible theoretical choices are CI procedures [6, 7] or valence bond (VB) calculations [25].

Conclusion

The validity of the HF picture in the binuclear Fe polycarbonyl complex **1** with respect to orbital fluctuations violating spatial and spin symmetry as well as the real character of the molecular orbitals has been investigated. It has been demonstrated that $|\Phi_0\rangle$ is clearly stable with respect to singlet fluctuations and complex solutions of the HF orbi-

Table 1. INDO results of the instability calculations on **1**. The orbital transitions contributing to the eigenvalues of the instability problem are given. The type and the Fe 3d character of the electron-hole pairs is also displayed. The type of the Fe 3d wave function corresponds to the metal-metal interaction. The eigenvalue problem has been obtained by means of a limited 14X10 CI. Cp: C_5H_5-moiety.

Type of Instability	i	λ_i (eV)	$\varphi_k \to \varphi_l$	%	MO-Type φ_k	% Fe 3d in φ_k	MO-Type φ_l	% Fe 3d in φ_l
Singlet	1	1.21	$14\,b_g \to 29\,b_u$	49.5	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$30\,a_g \to 17\,a_u$	15.7	Fe(δ), Cp(π), CO(σ)	64.9	Fe(π), CO(σ), Cp(π^*)	50.9
			$12\,b_g \to 29\,b_u$	9.3	Fe(δ), Cp(π), CO(π)	61.4	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$29\,a_g \to 17\,a_u$	7.6	Fe(σ), Cp(π)	62.1	Fe(π), CO(σ), Cp(π^*)	50.9
			$14\,b_g \to 30\,b_u$	5.7	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(σ^*), Cp(π^*)	36.0
	2	1.29	$30\,a_g \to 29\,b_u$	39.2	Fe(δ), Cp(π), CO(σ)	64.9	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$14\,b_g \to 17\,a_u$	19.0	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(σ), CO(σ), Cp(π^*)	50.9
			$30\,a_g \to 30\,b_u$	10.2	Fe(δ), Cp(π), CO(σ)	64.9	Fe(σ^*), Cp(π^*)	36.0
			$27\,b_u \to 33\,a_g$	6.7	Fe(δ^*), Cp(π)	71.3	Fe(σ), Cp(π^*)	33.0
Triplet (Non-singlet)	1	0.15	$14\,b_g \to 17\,a_u$	74.5	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(π), CO(σ), Cp(π^*)	50.9
			$13\,b_g \to 17\,a_u$	16.5	Fe(π^*), Cp(π)	60.3	Fe(π), CO(σ), Cp(π^*)	50.9
	2	0.44	$14\,b_g \to 29\,b_u$	75.6	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$13\,b_g \to 29\,b_u$	2.6	Fe(π^*), Cp(π)	60.3	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$30\,a_g \to 17\,a_u$	2.6	Fe(δ), Cp(π), CO(σ)	64.9	Fe(π), CO(σ), Cp(π^*)	50.9
Complex (Non-real)	1	1.11	$14\,b_g \to 29\,b_u$	60.6	Fe(π^*), CO(π^*), Cp(π)	22.4	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$30\,a_g \to 17\,a_u$	9.0	Fe(δ), Cp(π), CO(σ)	64.9	Fe(π), CO(σ), Cp(π^*)	50.9
			$12\,b_g \to 29\,a_u$	7.2	Fe(δ), Cp(π), CO(π)	61.4	Fe(π^*), CO(π^*), Cp(π^*)	36.0
			$29\,a_g \to 17\,a_u$	6.8	Fe(σ), Cp(π)	62.1	Fe(π), CO(σ), Cp(π^*)	50.9
	2	1.44	$31\,a_g \to 29\,b_u$	25.0	Fe(σ), Cp(π)	41.2	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$30\,a_g \to 29\,b_u$	17.4	Fe(δ), Cp(π), CO(σ)	64.9	Fe(σ^*), CO(π^*), Cp(π^*)	36.0
			$27\,b_u \to 33\,a_g$	16.6	Fe(δ^*), Cp(π)	71.3	Fe(σ), Cp(π^*)	33.0

tals. The many body variation corresponds to an angular correlation process and is of intraatomic short-range type. Due to the symmetry of the π^*(CO) transmitter orbitals long-range correlation of the left-right type is prevented. On the other hand an UHF solution in the vicinity of the spin-paired RHF determinant $|\Phi_0\rangle$ is predicted; the orbital excitation corresponds to an interfragment spin decoupling within a MO pair of π^* and π character (nature of the FeFe interaction). This decoupling mechanism is effectively transmitted via the π^* and (σ CO) valence orbitals of the bridging carbonyl groups. The significant delocalization of the $14\,b_g$ combination however prevents dramatical non-singlet instabilities.

Acknowledgement

This work has been supported by the Stiftung Volkswagen Werk.

[1] F. A. Cotton, Acc. Chem. Res. **11**, 225 (1978).

[2] P. S. Braterman, Struct. Bonding **10**, 57 (1971).

[3] M. Bénard, J. Amer. Chem. Soc. **100**, 7740 (1978); M. Bénard, Inorg. Chem. **18**, 2782 (1979).

[4] A. Mitschler, B. Rees, and M. S. Lehmann, J. Amer. Chem. Soc. **100**, 3390 (1978).

[5] G. Granozzi, E. Tondello, M. Bénard, and I. Fragala, J. Organomet. Chem. **194**, 83 (1980).

[6] M. F. Guest, I. H. Hillier, and C. D. Garner, Chem. Phys. Letters **48**, 587 (1977).

[7] M. Bénard and A. Veillard, Nouv. J. Chim. **1**, 97 (1977); M. Bénard, J. Amer. Chem. Soc. **100**, 2354 (1978).

[8] M. C. Böhm, Ber. Bunsenges. Phys. Chem. **85**, 755 (1981).

[9] M. C. Böhm, Chem. Phys. **60**, 277 (1981).

[10] M. C. Böhm, Theor. Chim. Acta **60**, 233 (1981).

[11] M. C. Böhm, Chem. Phys. Letters **81**, 284 (1981).

[12] D. J. Thouless, The Quantum Mechanics of Many Body Systems, Academic Press, New York 1961.

[13] J. Čiček and J. Paldus, J. Chem. Phys. **47**, 3976 (1967).

[14] M. C. Böhm and R. Gleiter, Theor. Chim. Acta **59**, 127 (1981).

[15] N. S. Ostlund, J. Chem. Phys. **57**, 2994 (1972).

[16] H. Fukutome, Prog. Theor. Phys. **47**, 1156 (1972).

[17] W. Kutzelnigg, Top. Curr. Chem. **40**, 31 (1973); A. C. Hurley, Introduction to the Electron Theory of Small Molecules, Academic Press, London 1976.

[18] M. J. S. Dewar and N. L. Hojvat (Sabelli), J. Chem. Phys. **34**, 1232 (1961); M. J. S. Dewar and N. L. Hojvat (Sabelli), Proc. Roy. Soc. Ser. A **264**, 431 (1961); M. J. S. Dewar and N. L. Sabelli, J. Phys. Chem. **66**, 2310 (1962); K. Ohno, Theor. Chim. Acta **3**, 219 (1964); G. Klopman, J. Amer. Chem. Soc. **86**, 4550 (1964).

[19] J. Paldus and A. Veillard, Mol. Phys. **35**, 445 (1978).
[20] M. Bénard and J. Paldus, J. Chem. Phys. **72**, 6546 (1980).
[21] M. Bénard, J. Chem. Phys. **71**, 2546 (1979).
[22] R. F. Byran and P. T. Greene, J. Chem. Soc. A **1970**, 3064.
[23] M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, Inorg. Chem. **15**, 1148 (1976).
[24] D. L. Thorn and R. Hoffmann, Inorg. Chem. **17**, 126 (1978).
[25] L. Noodleman and J. G. Norman. J. Chem. Phys. **70**, 4903 (1979); J. G. Norman, P. Barry-Ryan, and L. Noodleman, J. Amer. Chem. Soc. **102**, 4279 (1980).