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The ground state of $MoCr(O_2CH)_4$ at the *ab initio* SCF and CI levels. A symmetry adapted RHF energy functional with an artificial double minimum

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Ab initio restricted Hartree–Fock (RHF) calculations carried out on the ground state of $MoCr(O_2CH)_4$ lead to two distinct energy minima according to the initial guess made for the set of trial vectors. It is shown that these two symmetry-adapted wavefunctions can be correlated with a twofold degenerate broken-symmetry solution previously characterized for the related system of higher symmetry $Cr_2(O_2CH)_4$. Complete CI expansions have been carried out from either RHF polarized wavefunction using as a basis the set of eight frontier MO's with high metal character. These expansions yield poorly resymmetrized wavefunctions. A similar CI expansion has finally been carried out from a wavefunction resymmetrized at the SCF level and corresponding to a saddle point of the RHF energy hypersurface. The total energy associated with this latter expansion is the lowest obtained in the present work. The natural orbital analysis corresponds to $(\sigma)^{1.86}(\pi)^{3.58}(\delta)^{1.54}(\delta^*)^{0.46}(\pi^*)^{0.42}(\sigma^*)^{0.14}$ and shows that this resymmetrized CI expansion is in many respects similar to the correlated wavefunctions obtained for the homobinuclear parent systems.

Key words: $MoCr(O_2CH)_4$—*ab initio* SCF, CI—energy functional—double minimum

1. Introduction

The dimeric metal systems characterized with high formal bond orders such as 3, 3.5, 4 and 6 between the metal atoms have been the subject of increasing theoretical interest during the last ten years [1–3]. Concerning more specifically the nature of the bonding between two metal atoms populated each with four *d* electrons, *ab initio* SCF+CI investigations [1, 2, 6–14] did finally confirm the general validity of the quadruple bond scheme proposed by Cotton [4]. In fact, these studies have shown that the quadruple metal–metal bond was not always the strong interaction postulated in Cotton's early scheme. In fact, the coupling strength varies within a wide interval from the rather strong coupling of the "supershort" Cr-^{4}Cr bond [5] characterized with an important buildup of the electron deformation density [6], to the weak metal–metal interaction observed and computed in $Cr_2(O_2CR)_4$ [2, 7, 8]. In the latter case, the weak coupling of several electron pairs results in important correlation effects between metal *d*-valence electrons [8, 9] with the following consequences:

i) The correlation effects may alter the significance of the RHF results. In systems like $Cr_2(O_2CH)_4$, some RHF configurations for which *d*-electron correlation is partly or completely relieved may be found more stable than the quadruple bonding $\sigma^2\pi^4\delta^2$ configuration [10]. However, an adequate CI expansion always restores this latter configuration as the leading term [2, 7, 11, 12].

ii) they quantitatively modify the picture of the metal–metal quadruple bond obtained at the RHF level. When the correlation effects are included, the metal–metal interaction can be described in terms of four "strongly occupied" bonding MO's (σ, π and δ) and four "weakly occupied" antibonding MO's (σ^*, π^* and δ^*) [13]. The rise of the population of antibonding orbitals reduces – sometimes drastically – the formal bond order between the metal atoms [13].

iii) the strong correlation of metal *d* electrons in the all-bonding $\sigma^2\pi^4\delta^2$ configuration [4] can be traced to the lack of flexibility of this Hartree–Fock one-determinant wavefunction, due to spin- and space-symmetry constraints [8, 14]. The application to $Cr_2(O_2CH)_4$ and $Mo_2(O_2CH)_4$ of the stability equations derived by Čižek and Paldus [15] has produced several negative roots characteristic for singlet instability [8]. Some of the associated broken symmetry wavefunctions have been characterized [8].

Most calculations relative to the quadruple metal–metal bond have been carried out on homonuclear species of D_{4h} symmetry. For such systems considered at the RHF level, the all-bonding configuration can be assigned from symmetry considerations only. It is remarkable that the only calculation performed on a heterobinuclear complex of this type, namely $MoCr(O_2CH)_4$ (symmetry point group C_{4v}) yielded a RHF wavefunction which was quite different from those of both homonuclear parent molecules [12]. This result, obtained some years ago by one of us (M.B.) has not been clearly understood at that time. Since then, the results obtained by breaking the symmetry of the homonuclear D_{4h} systems [8] enticed us to complete and to reinterpret the results obtained for $MoCr(O_2CH)_4$.

2. The two RHF energy minima

The LCAO-MO-RHF calculations [16] have been performed at the experimental geometry of $MoCr(O_2CCH_3)_4$ (Fig. 1) with $d_{Mo-Cr} = 2.05$ Å [22]. The acetate ligands were modelized with formate groups.

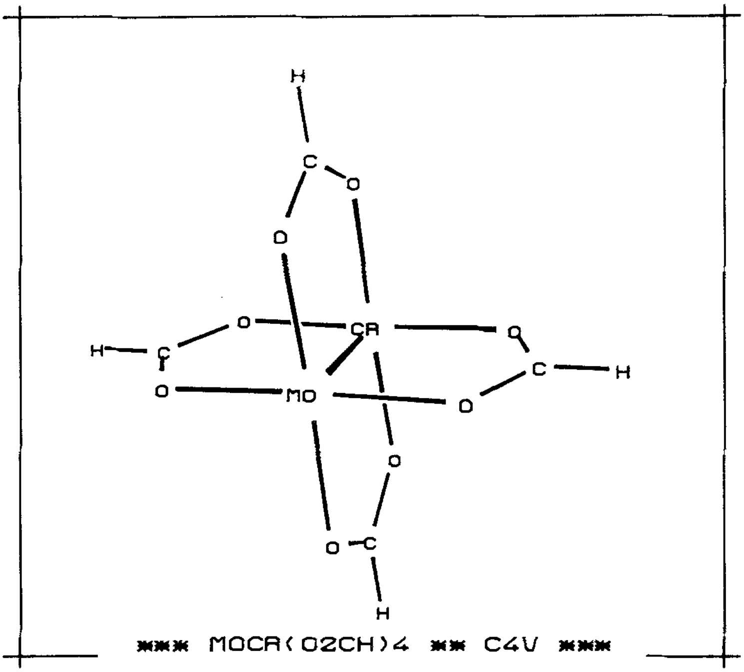

Fig. 1. The molecule $MoCr(O_2CH)_4$

The distribution of the d-valence electrons was adapted from the one leading in parent systems with D_{4h} symmetry to the quadruply bonding $\sigma^2\pi^4\delta^2$ configuration. One electron pair was attributed to the A_1 irreducible representation. Since this i.r. contains the combinations of the metal $d_{2z^2-x^2-y^2}$ orbitals which yield the σ bonding and antibonding MO's, this electron pair will be referred to as the "σ electron pair". Another pair, the "δ electron pair" was attributed to the B_2 i.r. which contains the d_{xy} orbital combinations. The remaining four d-valence electrons ("π electron pairs") were distributed in the degenerate E i.r. (d_{xz} and d_{yz} orbital combinations). *All* RHF *wavefunctions discussed in the present work correspond to this distribution.*

Two different sets of trial vectors have been used as starting points for the SCF iterations. These trial vectors have been induced from an analysis of the broken-symmetry wavefunctions of C_{4v} symmetry obtained for $Cr_2(O_2CH)_4$ [8] (see discussion in Sect. 4). In set I, the σ and δ pairs were localized on *molybdenum*, whereas the π pairs were localized on *chromium*. After convergence of the SCF process, the wavefunction $\psi_{RHF}(I)$ was obtained, characterized by an energy of -5761.4069 a.u. (Fig. 2) and orbital populations displayed in Table 1. In trial vector set II, a reverse localization scheme was chosen: the σ and δ pairs were localized on *chromium*, the π pairs on *molybdenum*. The SCF iterations yielded another solution, $\psi_{RHF}(II)$, corresponding to a total energy of -5761.4556 a.u. (Fig. 2) and orbital populations close to those of the trial set (Table 1). Therefore, wavefunctions $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ roughly transform into each other by an

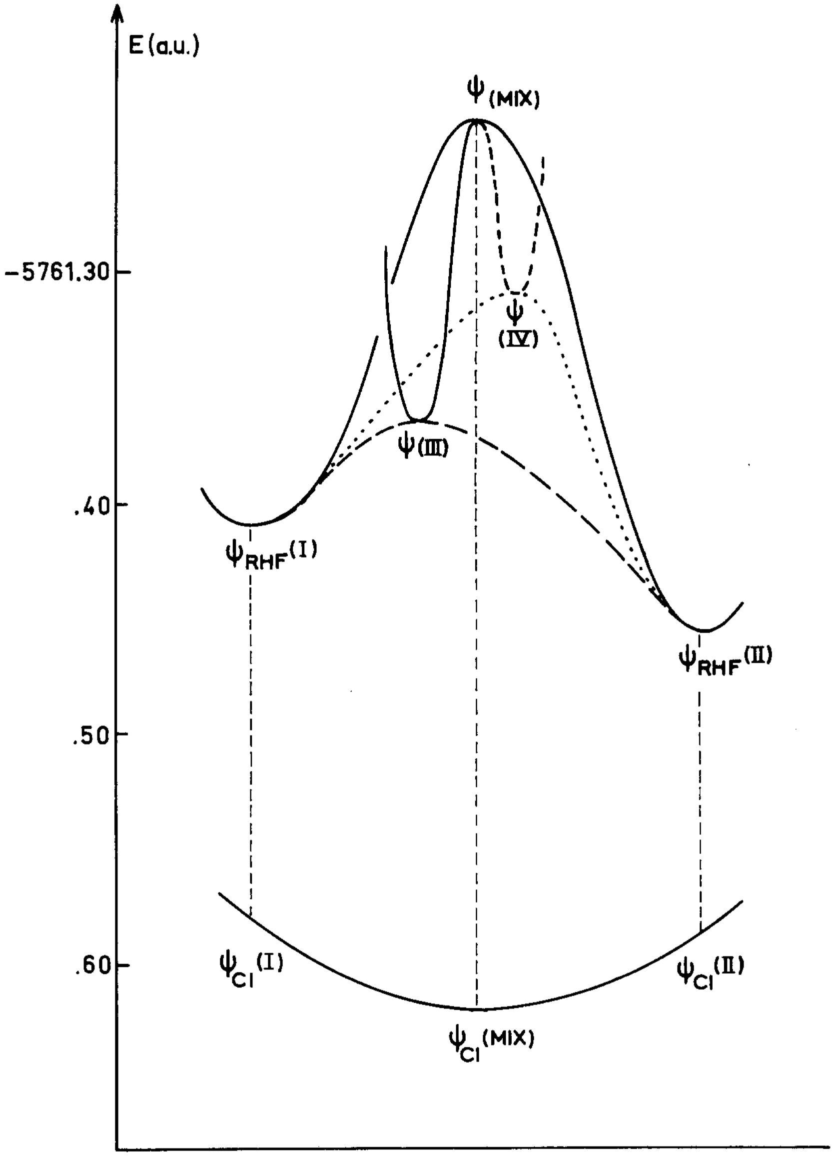

Fig. 2. Symmetry-adapted RHF energy hypersurface and CI energies for $MoCr(O_2CH)_4$

exchange between the four highest occupied metal MO's and the four lowest unoccupied ones.

3. The quadruply bonding configuration: a saddle point of the energy hypersurface

It may be noted that neither $\psi_{RHF}(I)$ nor $\psi_{RHF}(II)$ corresponds to the quadruply bonding configuration derived for $Cr_2(O_2CH)_4$ and $Mo_2(O_2CH)_4$ from a similar

Table 1. Total energy and *d* valence orbital populations for RHF and CI wavefunctions of $MoCr(O_2CH)_4$ and for RHF wavefunctions of $Cr_2(O_2CH)_4$

	Total energy (a.u.)	*d* valence orbital populations (from Mulliken population analysis)					
		d_{z^2}(Cr)	d_{z^2}(Mo)	d_{xy}(Cr)	d_{xy}(Mo)	d_{xz} d_{yz} (Cr)	d_{xz} d_{yz} (Mo)
		σ		δ		π	
$MoCr(O_2CH)_4$[a]							
$\psi_{RHF}(I)$	−5761.4069	0.387	1.593	0.099	1.958	3.784	0.334
$\psi_{RHF}(II)$	−5761.4556	1.807	0.250	1.976	0.129	0.464	3.614
$\psi_{RHF}(III)$	−5761.3361	0.341	1.642	1.957	0.165	2.195	1.903
$\psi_{RHF}(IV)$	−5761.3045	1.815	0.264	0.141	1.923	2.219	1.859
ψ(MIX)	−5761.2339	1.148	0.885	1.034	0.965	2.086	2.024
$\psi_{CI}(I)$	−5761.5805	0.492	1.507	0.832	1.328	3.132	1.008
$\psi_{CI}(II)$	−5761.5854	1.637	0.414	1.452	0.630	1.002	3.144
ψ_{CI}(MIX)	−5761.6193	1.131	0.900	1.022	1.014	2.088	2.066
$Cr_2(O_2CH)_4$[b]							
$(\sigma^2\pi^4\delta^2)$RHF (*s.a.*, D_{4h})	−2833.717	0.934		1.069		2.020	
broken-symmetry (C_{4v})	−2834.295	1.881 0.086		1.999 0.071		0.047 1.982	

[a] This work.

[b] Ref. [8]

distribution of the valence d electrons. The quadruply bonding configuration is characterized by a complete delocalization of each d electron pair on both metal atoms. In the systems with D_{4h} symmetry, $Cr_2(O_2CH)_4$ and $Mo_2(O_2CH)_4$, *this delocalization is imposed by the symmetry plane perpendicular to the metal–metal axis.* In $MoCr(O_2Ch)_4$, this specific symmetry element is abolished and symmetry adaptation is compatible with the localization of each electron pair on a given metal.

It has been noticed already that $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ correspond to the same localization scheme, the role of each metal atom being reversed. It therefore appears that the elusive "quadruply bonding configuration" corresponding to a complete delocalization of the four electron pairs, can be located halfway between $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ (Fig. 2). In order to investigate this region of the energy hypersurface, a new set of trial vectors was generated by Schmidt-orthonormalizing the orbital set resulting from the sum

$$\psi_0(\mathrm{MIX}) = \frac{1}{\sqrt{2}}[\psi_{RHF}(I) + \psi_{RHF}(II)].$$

The four d metal MO's are then delocalized on chromium and molybdenum. However, SCF iterations carried out from $\psi_0(\mathrm{MIX})$ resulted in a very long convergence process finally leading back to $\psi_{RHF}(II)$. During this process, the descent along the energy slope was rather unusual: very slow at the beginning, then faster, and then slow again in the vicinity of the RHF minimum. These results show that the quadruply bonding configuration does not correspond to a minimum of the symmetry adapted ground state energy of $MoCr(O_2CH)_4$. In fact, no local minimum is found in the vicinity of $\psi_0(\mathrm{MIX})$, except for $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$.

The characterization of two distinct minima on the ground state energy hypersurface of $MoCr(O_2CH)_4$ implies, for obvious topological reasons, the existence of at least one additional stationary state (Fig. 2). This stationary state – if unique – would correspond to a maximum, or more precisely to a saddle point located "between" the two minima. The existence of a third minimum corresponding to the quadruply bonding configuration and separated from $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ by two saddle points was not a priori excluded. However, the SCF convergence from $\psi_0(\mathrm{MIX})$ to $\psi_{RHF}(II)$ rules out this possibility. The only possible option remains the existance of a stationary state corresponding to a saddle point in the close vicinity of $\psi_0(\mathrm{MIX})$ [23] (Fig. 2). The unusual convergence rate of the SCF process starting from $\psi_0(\mathrm{MIX})$ supports this conclusion.

In order to improve the characterization of this stationary state, the trial vector set $\psi_0(\mathrm{MIX})$ was used for a constrained relaxation process, designed to minimize the energy without impairing the delocalization of valence d orbitals. This result was obtained from a sequence of SCF iteration steps during which the four unoccupied metal MO's were kept apart in an additional, dummy irreducible representation [24]. The obtained wavefunction $\psi(\mathrm{MIX})$ was associated with an energy of −5761.2339 a.u., destabilized by 0.17 and 0.22 a.u. with respect to the RHF minima.

4. Relation with the symmetry-adapted and broken-symmetry wavefunctions of $Cr_2(O_2CH)_4$

The role of spin- and space-symmetry constraints in the RHF energy minimization process of homobinuclear systems with a multiple metal–metal bond has been investigated in a previous work [8]. The possible occurrence of RHF and UHF configurations of lower energy and lower symmetry than the D_{4h} all-bonding configuration has been explored through the stability conditions derived by Čižek and Paldus [15]. For $Cr_2(O_2CH)_4$ at a Cr—Cr distance of 2.362 Å [26, 27], seven such "broken symmetry" solutions have been detected, and some of them characterized [8]. All these solutions belong to several subgroups of the real symmetry point group of the system D_{4h}. Two of them belong to the C_{4v} subgroup [28].

The lowest of these C_{4v} wavefunctions has been computed and characterized. It corresponds to the localization of the σ and π electron pairs on a given Cr atom and of the two π electron pairs on the other chromium. This solution is therefore twofold degenerate. A comparison between the d orbital populations obtained in Ref. [8] and in the present work (Table 1) shows that:

i) the twofold degenerate solution of C_{4v} symmetry obtained for $Cr_2(O_2CH)_4$ is similar to the wavefunctions $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ obtained for $MoCr(O_2CH)_4$

ii) in this latter case however, the lack of a symmetry plane between the two metals splits the twofold degenerate solution

iii) contrary to the case of $Cr_2(O_2CH)_4$ the localization of the d electron pairs in $MoCr(O_2CH)_4$ does not involve symmetry-breaking. All the wavefunctions investigated in the present work transform as the totally symmetric representation of the symmetry point group of $MoCr(O_2CH)_4$ (C_{4v}): these wavefunctions are symmetry-adapted.

A second negative root corresponding to a stationary state of C_{4v} symmetry had been found from the singlet instability subproblem of $Cr_2(O_2CH)_4$ [8]. No attempt had been made at that time to characterize this wavefunction. However, the direction of the steepest descent toward the solution can be deduced from the eigenvector associated with the Čižek–Paldus instability root [29]. According to this indication, the twofold degenerate stationary state related to this second root is expected to correspond to the localization of the σ electron pair on a given Cr atom, of the δ pair on the *other* Cr atom whereas the π pairs remain delocalized [8]. Trial vector sets $\psi_0(III)$ and $\psi_0(IV)$ corresponding to this localization scheme have been derived for $MoCr(O_2CH)_4$. The SCF iteration processes carried out from those trial vector sets finally yielded either $\psi_{RHF}(I)$ or $\psi_{RHF}(II)$ thus showing that no other symmetry adapted local minimum is present. However, this result did not rule out the possible existence of stationary states corresponding to saddle points – different from ψ(MIX) – on the energy hypersurface. To check this possibility, a constrained variational process was designed to retain the delocalization of the π electron pairs [30]. This constrained SCF process, carried out from $\psi_0(III)$ and $\psi_0(IV)$ yielded two solutions $\psi(III)$ and $\psi(IV)$ of respective energy −5761.3361 and −5761.3045 a.u. (Table 1). These energy values, intermediate between E(MIX) on the one hand, $E_{RHF}(I)$ and $E_{RHF}(II)$ on the other hand, indicate that $\psi(III)$ and $\psi(IV)$ are stationary states corresponding to additional saddle points on the energy hypersurface (Fig. 2) [31].

The quadruply bonding configuration resulting from the symmetry adapted RHF calculations carried out on $Cr_2(O_2CH)_4$ cannot be assimilated to a minimum of the energy functional. It corresponds to a saddle point which becomes accessible to the variational process because of the space symmetry constraints of the D_{4h} point group. A relief of these constraints yields a number of broken-symmetry solutions belonging to various point groups. Replacing $Cr_2(O_2CH)_4$ by an electronically equivalent, but heterobinuclear system relieves part of the symmetry constraints. The quadruply bonding stationary state still exists, but is not accessible anymore from a standard variation process. Artificial constraints must be introduced to stabilize it. Without such constraints, the variational process yields either of the two possible minima compatible with the C_{4v} symmetry, depending on the position of the initial vector set on the energy functional.

5. Configuration interaction expansions

The unusual RHF energy hypersurface obtained for $MoCr(O_2CH)_4$ can be represented as a couple of polarized wavefunctions minimizing the RHF energy, separated by a completely nonpolar and a couple of partly polarized stationary states. Polarized wavefunctions when available, may improve significantly the RHF energy [32] and often provide a better agreement with experiment [33]. However, they are much less suited to chemical interpretation than the nonpolar ones [34]. They need to be *resymmetrized* [35], either by means of projection techniques [36] or using CI expansions [37, 38].

We examine in the present work two different ways of resymmetrization by means of CI techniques. Configuration interaction expansions were first carried out on the valence d metal MO's of both polarized wavefunctions $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$. The eight d metal frontier MO's (4 occupied + 4 unoccupied [39]) were taken as a basis for a complete CI expansion (468 configurations). The two so-obtained correlated wavefunctions are very close in energy: $E_{CI}(I) = -5761.5805$ and $E_{CI}(II) = -5761.5854$ a.u. (Table 1, Fig. 2). The Mulliken population analysis shows that the CI expansions resulted in some indirect mixing between $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$. However, the d orbital populations issued from the two correlated wavefunctions $\psi_{CI}(I)$ and $\psi_{CI}(II)$ are still far from being similar (Table 1): they both retain some character of the original RHF wavefunction. Therefore, this type of CI expansion, carried out from either polarized RHF wavefunction, fails to provide a properly resymmetrized solution. The energy lowering associated with this relatively small expansion is however important: 0.13 to 0.17 a.u. indicating that the resymmetrization process involves *in this specific case* important correlation effects [40].

The wavefunction $\psi(\mathrm{MIX})$ obtained from a constrained relaxation of the normalized sum $\psi_{RHF}(I) + \psi_{RHF}(II)$, can be considered as a resymmetrized RHF wavefunction. It is unfortunately very poor in energy since the d electrons have

Table 2. Natural-orbital analysis of the CI wavefunctions obtained for $MoCr(O_2CH)_4$ (ψ_{CI}(MIX) and for some homobinuclear parent systems

		Natural-orbital population					
	d_{M-M}	σ	π	δ	δ^*	π^*	σ^*
ψ_{CI}(MIX) [a]	2.05	1.86	3.58	1.54	0.46	0.42	0.14
$Cr_2(O_2CH)_4$[13]	2.20	1.62	2.69	1.14	0.85	1.30	0.38
$Cr_2[H_2P(CH_2)_2]_4$[6]	1.885	1.92	3.59	1.39	0.61	0.41	0.08
$Mo_2(O_2CH)_4$[13]	2.09	1.89	3.69	1.65	0.35	0.31	0.11

[a] This work

been "forced" to delocalize on both metals. It therefore requires to be *repolarized* [35, 37] through an adequate CI expansion. The same complete CI expansion on the basis of the eight *d*-metal MO's, already used from $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$ was carried out on ψ(MIX). The resulting wavefunction ψ_{CI}(MIX) corresponds to an energy of −5761.6193 a.u. (Table 1) lower than both $E_{CI}(I)$ and $E_{CI}(II)$ by about 0.035 a.u. (Fig. 2). The correlation energy recovered from this expansion amounts 0.39 a.u., involving a major contribution of configurations higher than biexcited. The natural orbital analysis of the CI expansion in terms of bonding and antibonding MO's corresponds to

$$(\sigma)^{1.86}(\pi)^{3.58}(\delta)^{1.54}(\delta^*)^{0.46}(\pi^*)^{0.42}(\sigma^*)^{0.14}$$

thus yielding a decrease of the formal bond order from 4 to 2.98 (Table 2).

These results appear satisfactory since, at variance from the RHF results, the energetically best CI calculation obtained for $MoCr(O_2CH)_4$ is in many respects similar to the correlated wavefunctions obtained for the homobinuclear parent systems (Table 2). However, the repolarization, as the resymmetrization carried out through CI are both very slowly convergent processes since the CI is compelled to bring in the wavefunction a character which is missing in the reference RHF configuration [35, 37, 38]. The selected configurations active in these processes are likely to involve the complete set of MO's [37] and to require a large multireference basis. It can be therefore expected that an accurate CI description of the multiple metal–metal bond properties will require a very large computational effort, as illustrated by the recent calculations on the diatomic clusters with a sextuple bond, Cr_2 and Mo_2 [3].

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31. Several other paths could obviously be investigated between $\psi_{RHF}(I)$ and $\psi_{RHF}(II)$. More specifically, the delocalization of the σ and δ pairs coupled to an opposite localization of the two π pairs would probably yield other stationary states [8]. However, this localization scheme would break the symmetry of the wavefunction from C_{4v} to C_{2v}
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39. The metal character associated with a given *d* electron pair is sometimes scattered among several MO's of the canonical set. In order to improve the MO basis for the CI expansion, unitary transformations have been carried out on both the occupied and the virtual sets of MO's, using as a criterion the maximization of the metal weight in frontier orbitals.
40. For other problems, such as the description of core hole states [32, 33, 37] or the zwitterionic singlet excited state of nonsymmetric twisted polyenes [38], the RHF polar solutions represent perfectly reasonable approximations

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