

Orbital localization in transition metal molecules

Marten A. Buijse and Evert Jan Baerends

Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

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Abstract. In multiply bonded, weakly interacting systems the excessive electron repulsion associated with the non-dynamical correlation error can be reduced within the Hartree Fock approximation by localizing the bonding orbitals. The mechanism behind this (unphysical) orbital localization is studied through calculations on a model system, and SCF and CI calculations on the MnO^+ ion. It is shown, from a pair-population analysis of the two-particle density matrix (which is analogous to a Mulliken population analysis of the one-density) that the orbital localization is a two-electron effect. Transition metal molecules often exhibit this kind of orbital localization which may (*or may not*) require symmetry breaking. The special characteristics of transition metal molecules that makes them suitable candidates for orbital localization will be discussed.

Key words: Localized orbitals – Transition metal molecules

1. Introduction

Recently we studied the origin of the large weak-interaction Hartree Fock (HF) error in the ground state of the MnO_4^- ion and showed that, as a result, the bonding orbitals are localized, giving the individual bonds too much ionic character [1]. On the SCF (self consistent field) level, this unphysical orbital localization is difficult to detect because it does not require symmetry breaking. Furthermore, the weak-interaction error does not reveal itself through near degeneracy of bonding and antibonding orbitals. The HF function looks “normal”. In a configuration interaction (CI) calculation, however, the anomalous HF behaviour can be clearly demonstrated: covalency is restored as a result of considerable density changes while the non-dynamical correlation error is large (about 14 eV). This kind of HF behaviour has been studied before, but only in a few systems, and almost always in connection with symmetry breaking and HF instabilities [2–5]. The conditions that favour orbital localization (multiple bonding, small overlap and weak interaction and large on-site repulsion) are, however, not symmetry dependent and orbital localization can equally well occur in those systems in which there is no symmetry breaking to alert us [1].

In this paper we shall discuss the mechanism behind orbital localization by analysing, in section 2, the results of calculations on a simple but illustrative model system and, in section 3, the results of SCF and CI calculations on the "real" system MnO^+ . This ion is interesting because it also represents the group of transition metal molecules, in which the conditions that favour a large non-dynamical correlation error and orbital localization are already present at the equilibrium bond distance. Orbital localization, with or without symmetry breaking, will therefore not be rare in this group of molecules. In section 3, we shall discuss the special characteristics of the transition metal molecules, that make them suitable candidates for orbital localization. The conclusions are summarized in section 4.

2. Orbital localization in a model system

In this section we shall study and discuss the mechanism behind orbital localization, making use of a simple, homonuclear, model system, consisting of two atoms A and B, with N electrons in $N/2$ bonding orbitals. In evaluating the HF energy expressions we shall make some simplifying approximations that do not affect the essential characteristics of the model and are reasonable for the cases of small overlap and weak interaction that we are interested in.

In the model system, the AO (atomic orbital) ϕ_i^A on center A will overlap with one orbital ϕ_i^B , on center B, i.e., $\langle \phi_i^A | \phi_j^B \rangle = 0$ if $i \neq j$. It is further assumed that the overlap $M = \langle \phi_i^A | \phi_i^B \rangle$ is equal for all i . From the two sets of AO's $\{\phi^A\}$ and $\{\phi^B\}$ we can then construct $N/2$ (delocalized) bonding orbitals χ_i and $N/2$ (delocalized) antibonding orbitals χ_i^*

$$\chi_i = \frac{1}{\sqrt{2+2M}} (\phi_i^A + \phi_i^B), \quad \chi_i^* = \frac{1}{\sqrt{2-2M}} (\phi_i^A - \phi_i^B). \quad (1)$$

By making linear combinations of χ_i and χ_i^* we can construct (broken symmetry) orbitals that are (partly) localized on either A or B

$$\varphi_i = \cos(\mu_i)\chi_i + \sin(\mu_i)\chi_i^* = a_i\phi_i^A + b_i\phi_i^B, \quad (2)$$

with a_i and b_i given by

$$a_i = \frac{\cos \mu_i}{\sqrt{2+2M}} + \frac{\sin \mu_i}{\sqrt{2-2M}}, \quad b_i = \frac{\cos \mu_i}{\sqrt{2+2M}} - \frac{\sin \mu_i}{\sqrt{2-2M}}. \quad (3)$$

The degree of localization is determined by the angle μ_i . If $\mu_i = 0$ ($a_i = b_i$) or $\mu_i = \pm \frac{1}{2}\pi$ ($a_i = -b_i$) then φ_i is completely delocalized, while the bond is completely localized on center A or B if $\cos \mu_i / \sqrt{2+2M} = \pm \sin \mu_i / \sqrt{2-2M} = \frac{1}{2}$; if we neglect overlap then this is the case if $\mu_i = \pm \frac{1}{4}\pi$.

We now define a HF function, built from these orbitals, $\Psi(1 \cdots N) = |\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2 \cdots|$, and calculate expressions for the one- and two-electron energy, which are both parametrically dependent on the localization parameters μ_i . Note that each bond (labeled with the index i) contains just two electrons, so only one orbital (either delocalized or localized) is occupied per bond.

One-electron energy

In the expression for the one-electron energy $E^{(1)}$, for simplicity we shall use the following approximations in our model system:

$$\begin{aligned} h^{AA} &= h^{BB} = \langle \phi_i^A | \hat{h} | \phi_i^A \rangle = \langle \phi_j^A | \hat{h} | \phi_j^A \rangle. \\ h^{AB} &= \langle \phi_i^A | \hat{h} | \phi_i^B \rangle = \langle \phi_j^A | \hat{h} | \phi_j^B \rangle, \end{aligned} \quad (4)$$

i.e., all bonds have comparable strength in the model system. $E^{(1)}$ can be calculated from the one-electron density

$$\begin{aligned} \varrho(1', 1) &= \sum_{i=1}^{\frac{1}{2}N} 2\varphi_i(1')\varphi_i(1) \\ &= \sum_{i=1}^{\frac{1}{2}N} 2a_i^2 \phi_i^A(1')\phi_i^A(1) + \sum_{i=1}^{\frac{1}{2}N} 2b_i^2 \phi_i^B(1')\phi_i^B(1) \\ &\quad + \sum_{i=1}^{\frac{1}{2}N} 2a_i b_i [\phi_i^A(1')\phi_i^B(1) + \phi_i^B(1')\phi_i^A(1)]. \end{aligned} \quad (5)$$

If we define the constants ϱ^A , ϱ^B , and ϱ^{AB} as

$$\varrho^A = \sum_{i=1}^{\frac{1}{2}N} 2a_i^2, \quad \varrho^B = \sum_{i=1}^{\frac{1}{2}N} 2b_i^2, \quad \varrho^{AB} = \sum_{i=1}^{\frac{1}{2}N} 4a_i b_i \quad (6)$$

then the one-electron energy can be expressed as

$$E^{(1)} = \sum_{i=1}^{\frac{1}{2}N} 2\langle \varphi_i | \hat{h} | \varphi_i \rangle = \varrho^A h^{AA} + \varrho^B h^{BB} + \varrho^{AB} h^{AB} = \sum_{i=1}^{\frac{1}{2}N} E_i^{(1)}, \quad (7)$$

with

$$E_i^{(1)} = \frac{2(h^{AA} - h^{AB})}{1 - M} - \cos^2 \mu_i \frac{4(Mh^{AA} - h^{AB})}{1 - M^2}.$$

The lowest value of $E_i^{(1)}$ is reached when

$$\cos \mu_i = 1 \left\{ \varphi_i = \chi_i, E_i^{(1)} = \frac{2(h^{AA} + h^{AB})}{1 + M} \right\}$$

or

$$\cos \mu_i = 0 \left\{ \varphi_i = \chi_i^*, E_i^{(1)} = \frac{2(h^{AA} - h^{AB})}{1 - M} \right\},$$

depending on the sign of $Mh^{AA} - h^{AB}$ (if the phases are chosen such that $M > 0$, this term will usually be positive). The minimum in the total one-electron energy is therefore reached when all orbitals are delocalized and symmetry adapted. Breaking the symmetry and localizing one or more orbitals will always lead to an increase of the one-electron energy. Only if $Mh^{AA} - h^{AB} = 0$, which is e.g. the case at long internuclear distance where both the overlap and the interaction are zero, is the one-electron energy independent of the degree of localization. We can conclude that symmetry breaking and orbital localization are two-electron effects.

Two-electron energy

The electron repulsion energy $E^{(2)}$ is determined by the two-particle density

$$\Gamma^{(2)}(1, 2) = 2 \sum_{i,j=1}^{\frac{1}{2}N} \varphi_i(1)\varphi_i(1)\varphi_j(2)\varphi_j(2) - \sum_{i,j=1}^{\frac{1}{2}N} \varphi_i(1)\varphi_j(1)\varphi_i(2)\varphi_j(2). \quad (8)$$

For our purposes, it is very useful to analyse $\Gamma^{(2)}(1, 2)$ in a way that is analogous to a Mulliken population analysis [6] of the one-electron density, $\varrho(1)$. In a Mulliken analysis, the N electrons in the molecule are divided over the various atoms. To do this, $\varrho(1)$ is expressed in the AO basis and each product $\varrho_{ij}^{AB}\phi_i^A(1)\phi_j^B(1)$ contributes $\frac{1}{2}\varrho_{ij}^{AB}\langle\phi_i^A|\phi_j^B\rangle$ to the population of both the atoms A and B (note that this is also correct if $A \equiv B$; the total contribution to the population of atom A is in that case equal to $\varrho_{ij}^{AA}\langle\phi_i^A|\phi_j^B\rangle$). The two-density $\Gamma^{(2)}(1, 2)$ is a *pair*-probability and we are concerned with the problem of dividing $\frac{1}{2}N(N-1)$ electron pairs. We can distinguish between two types of electron pairs: on-site pairs with both electrons on the same center and inter-atomic pairs, with the two electrons on two different centers. The symbol Γ will be used for the pair-population, Γ_{AA} being the number of on-site pairs with both electrons on center A and Γ_{AB} the number of inter-atomic pairs with one electron on A and one on B. If $\Gamma^{(2)}(1, 2)$ is expressed in the AO basis, the product $\Gamma_{ijkl}^{(2)ABCD}\phi_i^A(1)\phi_j^B(1)\phi_k^C(2)\phi_l^D(2)$ contributes $\frac{1}{4}\Gamma_{ijkl}^{(2)ABCD}\langle\phi_i^A|\phi_j^B\rangle\langle\phi_k^C|\phi_l^D\rangle$ to each of the pair populations Γ_{AC} , Γ_{AD} , Γ_{BC} and Γ_{BD} . The total number of electron pairs is, of course, always equal to $\sum_A \Gamma_{AA} + \sum_{A>B} \Gamma_{AB} = \frac{1}{2}N(N-1)$. This pair-population analysis is especially useful in case of HF functions because, as we will see below, the source of the non-dynamical or molecular HF error can be traced back to an incorrect ratio of on-site and inter-atomic pairs.

In calculating an expression for the two-electron energy $E^{(2)}$ in the model system we make the following approximations for the two-electron integrals:

$$\begin{aligned} J_{AA} &= J_{BB} = [\phi_i^A\phi_i^A, \phi_i^A\phi_i^A] = [\phi_i^A\phi_i^A, \phi_j^A\phi_j^A] = [\phi_j^A\phi_j^A, \phi_j^A\phi_j^A] \\ J_{AB} &= [\phi_i^A\phi_i^A, \phi_j^B\phi_j^B] = [\phi_i^A\phi_i^A, \phi_j^B\phi_j^B] = [\phi_j^A\phi_j^A, \phi_j^B\phi_j^B]. \end{aligned} \quad (9)$$

We will further neglect the two-electron integrals of the type $[\phi^A\phi^A, \phi^A\phi^B]$, $[\phi^A\phi^B, \phi^B\phi^B]$ and $[\phi^A\phi^B, \phi^A\phi^B]$, and also the exchange integrals $[\phi_i^A\phi_j^A, \phi_i^A\phi_j^A]$, $[\phi_i^A\phi_j^A, \phi_i^B\phi_j^B]$ and $[\phi_i^B\phi_j^B, \phi_i^B\phi_j^B]$. These integrals are often more than an order of magnitude smaller than the Coulomb integrals J_{AA} , J_{AB} and J_{BB} , especially if the overlap is small.

The expression for the electron repulsion energy $E^{(2)}$ is then given by

$$E^{(2)} = \int \frac{\Gamma^{(2)}(1, 2)}{r_{12}} d1d2 = \Gamma_{AA}J_{AA} + \Gamma_{BB}J_{BB} + \Gamma_{AB}J_{AB}, \quad (10)$$

with the on-site pair-populations Γ_{AA} and Γ_{BB} and the inter-atomic pair-population Γ_{AB} given by

$$\begin{aligned} \Gamma_{AA} &= \sum_{i=1}^{\frac{1}{2}N} a_i^2 + 4 \sum_{i,j>i}^{\frac{1}{2}N} a_i^2 a_j^2, & \Gamma_{BB} &= \sum_{i=1}^{\frac{1}{2}N} b_i^2 + 4 \sum_{i,j>i}^{\frac{1}{2}N} b_i^2 b_j^2, \\ \Gamma_{AB} &= \sum_{i=1}^{\frac{1}{2}N} 2a_i^2 b_i^2 + 4 \sum_{i,j>i}^{\frac{1}{2}N} (a_i^2 b_j^2 + b_i^2 a_j^2). \end{aligned} \quad (11)$$

(Note that Eqs. (11) only approximately hold in case of non-zero overlap, due to the neglect of products of type $\phi^A(1)\phi^A(1)\phi^A(2)\phi^B(2)$ and

$\phi^A(1)\phi^B(1)\phi^A(2)\phi^B(2)$ in $\Gamma^{(2)}(1, 2)$.) In the HF approximation, the total number of on-site electron pairs will generally be too high, leading to too much electron repulsion because an on-site electron pair represents more repulsion than an inter-atomic pair ($J_{AA} > J_{AB}$). This is the well known (non-dynamical) HF error [7]. It is especially large in the case of large internuclear distance where $J_{AB} \approx 0$. Because the total number of on-site pairs $\Gamma_{AA} + \Gamma_{BB}$ depends on the localization parameters μ_i , the HF wavefunction can control, within certain boundaries, the magnitude of the HF error by localizing one or more of the orbitals. Whether the orbitals will actually come out localized is, of course, not determined by the magnitude of the HF error alone but also by the energy stabilization associated with the interaction. As we saw earlier, the one-electron contribution to the total interaction energy will, in general, profit from orbital *delocalization*. The degree of localization will therefore depend on the magnitude of the HF error, *relative* to the total interaction energy.

For the case of zero overlap and interaction, the one-electron energy is no longer dependent on the degree of localization and the HF error is the only contribution to the total interaction energy. The total number of on-site electron pairs is in this case given by

$$\begin{aligned} \Gamma_{AA} + \Gamma_{BB} &= \sum_{i=1}^{\frac{1}{2}N} (a_i^4 + b_i^4) + 4 \sum_{i,j>i}^{\frac{1}{2}N} (a_i^2 a_j^2 + b_i^2 b_j^2) \\ &= \frac{1}{4}N(N-1) + \left[\frac{1}{2} \sum_{i=1}^{\frac{1}{2}N} \sin^2 2\mu_i + 2 \sum_{i,j>i}^{\frac{1}{2}N} \sin 2\mu_i \sin 2\mu_j \right]. \end{aligned} \quad (12)$$

It is clear from Eq. (12) that in the single-bond case the number of on-site electron pairs (and the electron repulsion energy) is minimal if $\mu_i = 0$, corresponding to a bond that is delocalized and symmetry adapted. In multiply bonded systems, however, the HF wavefunction can lower the electron repulsion energy by breaking the symmetry and localizing one or more bonding orbitals. In Table 1, the number of on-site and inter-atomic electron pairs are compared for the HF function with delocalized (or symmetry adapted, SA) orbitals and the HF function with localized (or broken symmetry, BS) orbitals. In the BS case, the localization is chosen in such a way as to minimize the total number of on-site electron pairs. Note that with an odd number of bonds, the lowest energy is reached if one of the orbitals stays delocalized, a result that was also found by Lepetit et al. in their calculations on N_2 [5]. The exact (or full CI) values are also listed in Table 1. These exact values can be easily calculated because, in this case of zero overlap and interaction, the electrons will always be divided evenly over the two atoms due to correlation. In the SA HF case, the number of on-site electron pairs is too high, compared to the exact values (Table 1). This is precisely what is meant when we say that the HF wavefunction puts too much weight on ionic configurations. Note that the error increases with the number of bonds. If broken symmetry solutions are not allowed, or if there is only a single bond, then the number of on-site electron pairs and the electron repulsion energy can only be lowered by correlating the movement of the electrons in a CI calculation. If, however, broken symmetry orbitals are allowed and we have a multiply bonded system, then the electron-repulsion energy can always be lowered on the HF level by localizing the orbitals. For an even number of bonding orbitals we can even reach the exact number of on-site pairs if we localize half of the orbitals on center A and the other half on center B.

Table 1. Total number of on-site and inter-atomic electron pairs for exact (full CI), symmetry adapted (SA) HF and broken symmetry (BS) HF functions, in a homonuclear model system with N electrons in $\frac{1}{2}N$ bonds and zero overlap and interaction

Bonds	Electron pairs	exact		SA HF ($\mu_i = 0$)		μ	BS HF	
		$\Gamma_{AA} + \Gamma_{BB}$	Γ_{AB}	$\Gamma_{AA} + \Gamma_{BB}$	Γ_{AB}		$\Gamma_{AA} + \Gamma_{BB}$	Γ_{AB}
1	1	0	1	$\frac{1}{2}$	$\frac{1}{2}$	$\{\mu_1 = \frac{1}{4}\pi$	1	0}
2	6	2	4	3	3	$\mu_1 = \frac{1}{4}\pi$ $\mu_2 = -\frac{1}{4}\pi$	2	4
3	15	6	9	$7\frac{1}{2}$	$7\frac{1}{2}$	$\mu_1 = \frac{1}{4}\pi$ $\mu_2 = -\frac{1}{4}\pi$ $\mu_3 = 0$	$6\frac{1}{2}$	$8\frac{1}{2}$
4	28	12	16	14	14	$\mu_1 = \frac{1}{4}\pi$ $\mu_2 = \frac{1}{4}\pi$ $\mu_3 = -\frac{1}{4}\pi$ $\mu_4 = -\frac{1}{4}\pi$	12	16
$\frac{1}{2}N$	$\frac{1}{2}N(N-1)$	$\frac{1}{4}N(N-2)$	$\frac{1}{4}N^2$	$\frac{1}{4}N(N-1)$	$\frac{1}{4}N(N-1)$			

In the case of non-zero overlap, the total number of on-site electron pairs will also depend on the overlap M . We analyse this dependency in a double-bond system in which the two bonds are allowed to localize in opposite directions, with localization parameter $\mu = \mu_1 = -\mu_2$. In Fig. 1, the total number of on-site electron pairs, $\Gamma_{AA} + \Gamma_{BB}$, is plotted as a function of μ , for several values of the overlap M . Although the calculated value of $\Gamma_{AA} + \Gamma_{BB}$ [using Eqs. (11)] is only approximately equal to the *exact* number of on-site electron pairs if $M \neq 0$, Fig. 1 gives a good indication of what happens: the stabilization in electron repulsion energy, due to localization, is smaller for larger overlap. As far as the electron repulsion energy is concerned, the tendency to localize the orbitals will therefore decrease with increasing overlap.

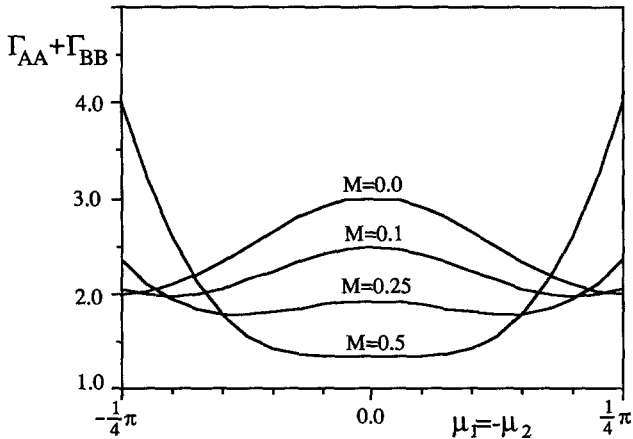


Fig. 1. Total number of on-site electron pairs as a function of localization in a double bond system with $\mu = \mu_1 = -\mu_2$ and for several values of the overlap M

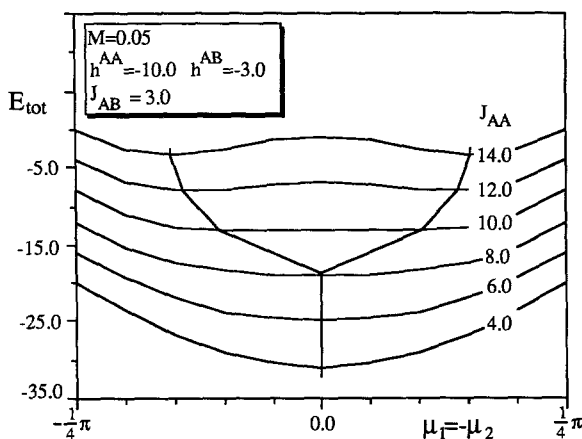


Fig. 2. Total energy $E = E^{(1)} + E^{(2)}$ as a function of localization in a double bond system with $\mu = \mu_1 = -\mu_2$ and for several values of the on-site repulsion integral J_{AA} . Connecting lines are drawn through the minima in the $E(\mu)$ curves

The magnitude of the HF error not only depends on the number of on-site electron pairs but also on the value of the on-site and inter-atomic repulsion integrals J_{AA} and J_{AB} . In Fig. 2 the total energy $E = E^{(1)} + E^{(2)}$ is plotted (for the double-bond system discussed above) as a function of localization for several values of the on-site integral J_{AA} . The quantities M , h^{AA} , h^{AB} and J_{AB} are assigned values so that the model represents a weakly interacting system. These quantities are kept constant, only J_{AA} is varied. It is clear from Fig. 2 that at small values of J_{AA} the lowest energy is reached when the orbitals are delocalized ($\mu = 0$) and that localization becomes profitable at larger values of J_{AA} . It is interesting to note the relative insensitivity of the total energy to the degree of localization. Especially with J_{AA} values around 10.0, the energy of the SA function with delocalized orbitals is about equal to the energy of the BS function with localized orbitals.

Homonuclear systems, like the model system discussed above are advantageous because a large weak-interaction HF error can often be diagnosed at the SCF level: if the HF function is optimized without symmetry constraints, the HF error and associated orbital localization may reveal itself directly through symmetry breaking. If we prevent orbital localization (by the simple requirement that the orbitals are symmetry adapted), the presence of a considerable HF error can be determined from an analysis of the roots of the singlet instability matrix [8] or from the near degeneracy of bonding and antibonding orbitals (the non-dynamical correlation error is often called the near-degeneracy correlation error).

The conditions that favour a large HF error and orbital localization (multiple bonding, small overlap/weak interaction and large on-site repulsion) are, however, not symmetry dependent and can equally well occur in (hetero-nuclear) systems where the orbitals can localize without breaking the symmetry [1, 3, 4]. In these systems, there is no way in which we can prevent the unphysical localization of the bonding orbitals. Furthermore, the large HF error will often go unnoticed because it does not reveal itself through near degeneracy of bonding and antibonding orbitals or through negative roots of the singlet instability matrix. However, also in systems where there is no symmetry breaking to alert us, we should beware of unwarranted localization effects at the HF level. These are,

just as symmetry breaking is when there is symmetry to be broken, an indication of a considerable weak-interaction HF error that has to be remedied by CI.

3. Orbital localization in transition metal molecules

In this section we shall present and discuss the results of some minimal basis SCF and CI calculations on MnO^+ with a twofold purpose: to corroborate the model-system results, discussed in the previous section and to illustrate the special characteristics of transition metal systems that make them suitable candidates for orbital localization. The MnO^+ ion is a hetero-nuclear, triply bonded, closed shell molecule with SCF configuration $\cdots\pi^4\sigma^2\delta^4$. The σ and π bonds are linear combinations of overlapping Mn_{3d} and O_{2p} orbitals, while the δ orbitals are pure metal $3d$. In the CI calculations, each bond is represented by a linear combination of the three possible configurations ($\phi\phi$, $\phi\phi^*$ and $\phi^*\phi^*$) in the space of bonding and antibonding orbitals. It is clear that a wavefunction constructed in this way will properly describe dissociation [9]. In MnO^+ , with three bonds, the total number of configurations is then $3^3 = 27$.

The origin of the large HF error in transition metal systems can be traced back to the limited spatial extension of the metal $3d$ shell, which is about the same size as the $3s/3p$ shell although the latter is much lower in energy and often considered core-like. Pauli (or closed shell) repulsion between ligand orbitals that overlap with the $3d$ orbitals to form a bond and the $3s/3p$ shell will then prevent the internuclear distance becoming small enough for efficient overlap and interaction. A detailed analysis of this problem can be found elsewhere [1]. A second reason for the small overlap is the nodal structure of the $3d$ orbitals preventing the overlap reaching a large value, even at internuclear distances that are much smaller than the equilibrium distance. This is illustrated in Fig. 3, where the overlap in σ and π symmetry is shown for MnO^+ , as function of Mn-O distance. In the π symmetry the poor overlap at R_e is caused by the long Mn-O distance, while the small overlap in the σ symmetry is also a result of the nodal structure of the overlapping $2p$ and $3d$ orbitals. The inefficient overlap is directly responsible for the weak interaction and large HF error, the magnitude of which is further

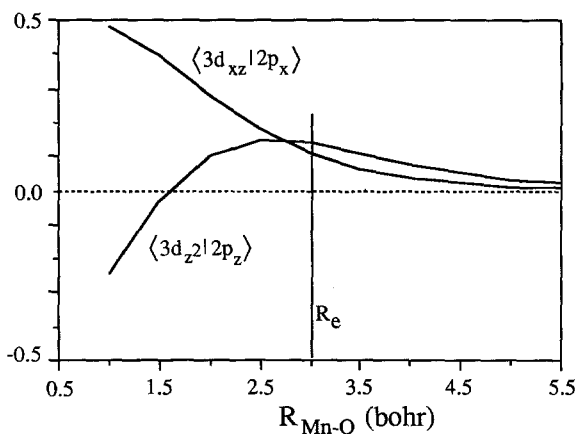


Fig. 3. Overlap between Mn $3d$ and O $2p$ orbitals as a function of Mn-O distance. R_e is the calculated equilibrium distance for the MnO^+ ion

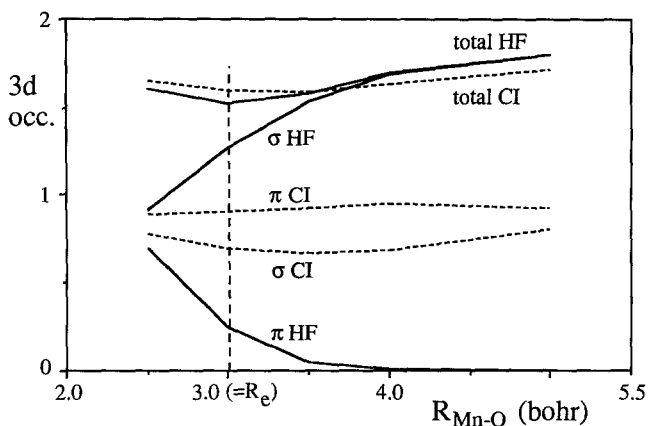


Fig. 4. Mn 3d occupation in orbitals of σ and π symmetry and total 3d occupation in the MnO^+ ion as a function of Mn-O distance. In the π symmetry, the total ($\pi_x + \pi_y$) occupation is shown

increased by the relatively large on-site $3d$ - $3d$ repulsion (due to the compact nature of the $3d$ orbitals) and the multiple bonding involving $3d$. The result is shown in Fig. 4 where the Mulliken $3d_\sigma$ and $3d_\pi$ occupations are displayed as function of internuclear distance: the σ and π orbitals localize, the σ on the metal and the π on the oxygen, if the Mn-O distance increases. It is further clear that at the equilibrium distance R_e the localization is already substantial but not complete. The unrealistic HF behaviour can be clearly demonstrated by comparing with the CI results. At the CI level, the $3d_\sigma$ and $3d_\pi$ occupations do not change much over the range of Mn-O distances considered and the σ and π bonds show little localization (Fig. 4). The total calculated correlation energy at R_e is $\Delta E = E^{\text{CI}} - E^{\text{HF}} = -5.5$ eV; the changes in the individual contributions $E^{(1)}$ and $E^{(2)}$ are much larger: -38.0 eV and $+32.5$ eV respectively. It is a surprising result that the electron repulsion energy $E^{(2)}$ increases if electron correlation is introduced. A decrease in $E^{(2)}$ is generally expected upon inclusion of CI as electrons are thought to be better able to avoid each other. In this case, however, the HF wavefunction already avoided too much repulsion by localizing the orbitals. In the CI wavefunction covalency is restored at the expense of increasing electron-electron repulsion. Changes in the density matrix, due to the reintroduction of orbital delocalization and covalency, are responsible, through changes in $E^{(1)}$, for the lowering of the total energy.

It is interesting to note that these changes do not affect the total 3d ($\sigma + \pi$) occupation, which is about the same for HF and CI wavefunctions (Fig. 4) and, furthermore, is remarkably constant over the range of Mn-O distances considered. The same result was found in the MnO_4^- system [1]. To explain this phenomenon, we show in Fig. 5 the total HF energy as a function of $3d_\sigma$ and $3d_\pi$ occupation. This total energy was calculated from a determinant with σ and π "bonding orbitals" given by: $\varphi_\sigma = a_\sigma \text{Mn}_{3d\sigma} + b_\sigma \text{O}_{2p\sigma}$ and $\varphi_\pi = a_\pi \text{Mn}_{3d\pi} + b_\pi \text{O}_{2p\pi}$. By varying the coefficients a and b , the $3d_\sigma$ and $3d_\pi$ occupation can be controlled. As a visual aid, we also plotted some lines along which the total 3d occupation is constant. It is clear from Fig. 5 that the total energy is very sensitive to density variations that affect the distribution of density over the various sites and involve changes in the total 3d occupation. In fact, the energy change associated with only a small change in total 3d occupation is larger than the total correlation energy. As a result, the total 3d occupation

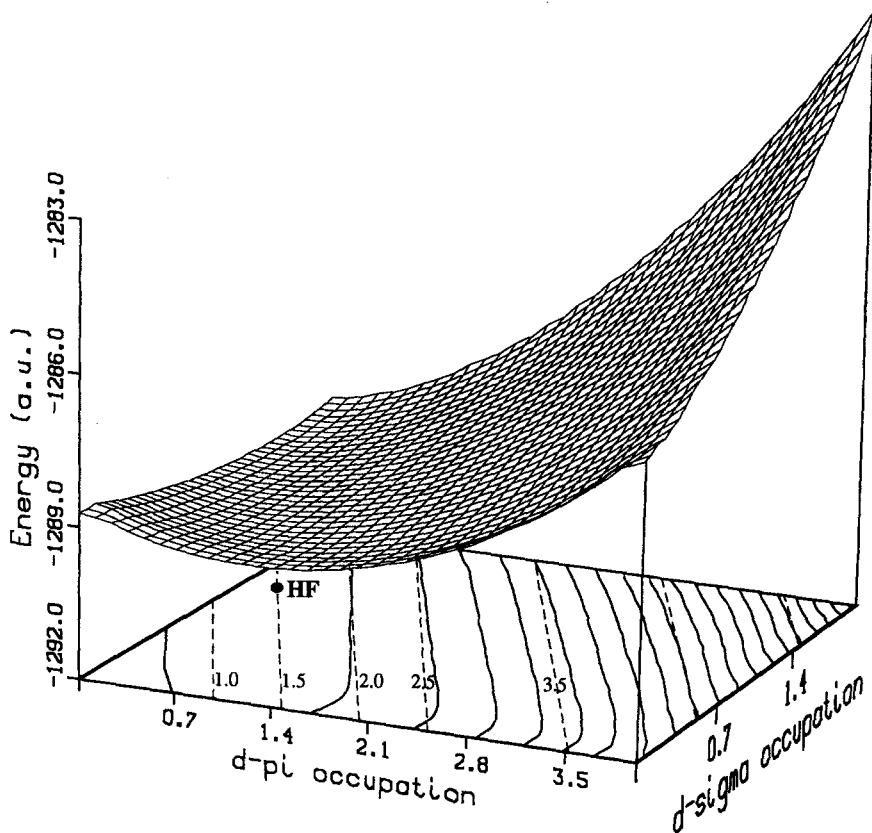


Fig. 5. MnO^+ energy surface and projected contours for a determinant with localized σ and π orbitals, as a function of localization. Lines with constant total $3d$ occupation are also drawn. The HF energy is reached when the σ and π occupations are equal to 1.22 and 0.28 respectively

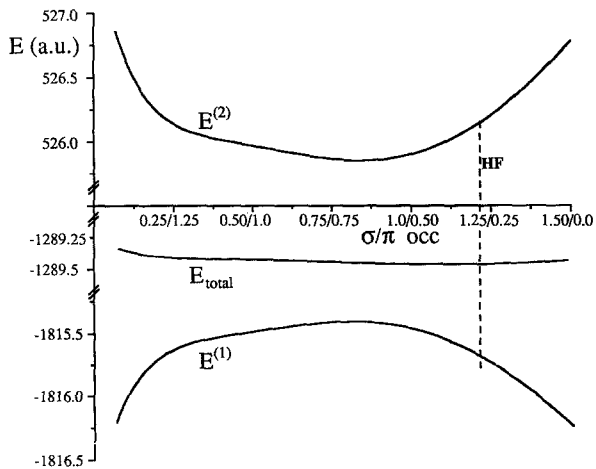


Fig. 6. MnO^+ energy values for a determinant with localized σ and π orbitals, as a function of localization. The total $3d$ occupation is kept constant at the HF (and CI) value of 1.5

predicted by HF theory will not differ much from the CI (or exact) value. In a multiply bonded system, however, the HF wavefunction has some additional freedom because the orbitals can be localized (to reduce the electron repulsion energy) *without* changing the total $3d$ occupation, something that is not possible with only a single bond. The energy variations associated with this kind of density changes are very small (Fig. 5). In Fig. 6 we show the energy as a function of localization when the total $3d$ occupation is kept constant at 1.5, which is the HF (and CI) value. It is clear from this plot that the one- and two-electron energy terms are very sensitive to changes in the degree of localization. The total energy curve, however, is very flat with energy variations that are much smaller than the magnitude of the HF error. At the minimum, the HF orbitals are strongly localized, but the energy difference with a function with σ and π orbitals that are delocalized to the same extent ($3d_e$ occupation is 0.5, total $3d_e$ occupation is 1.0) is less than 1 eV.

It is interesting to note that the invariance of the total $3d$ occupation discussed above has been observed before in the MnO_4^- system, in situations where the *formal* number of $3d$ electrons is changed by charge transfer type excitations or by adding one or even two electrons [10, 11]. This phenomenon cannot be satisfactorily explained by the compact nature (and corresponding high repulsion) of the $3d$ orbitals because the Mn $3d$ - $3d$ repulsion is not much larger than the O $2p$ - $2p$ repulsion ($J_{3d,3d} \approx 0.8$ a.u., $J_{2p,2p} \approx 0.7$ a.u.). Furthermore, addition of an extra $3d$ electron to the MnO^+ system results in an MnO wavefunction in which the extra electron is divided about equally over the two atoms, corresponding to a change in $3d$ occupation of about 0.5 electron. The remarkable invariance of the total $3d$ occupation in the four-coordinated system can, however, be explained from a pair-population analysis as described in section 2 and can be traced back to the fact that the total number of on-site electron pairs varies as N^2 . Of the 10 bonding electrons in MnO_4^- , about 5 will be on the metal and $\frac{5}{4}$ will be on (on average) each of the four oxygens. Adding one extra electron to the metal increases the number of on-site $3d$ - $3d$ pairs from $\frac{1}{2}5(5-1)$ to $\frac{1}{2}6(6-1)$ and we have an increase in (on-site) electron repulsion, equal to $5J_{3d,3d}$. Adding the extra electron to the oxygens will also increase the total number of oxygen-oxygen electron pairs by 5. However, not all will be on-site oxygen pairs because the extra electron is divided over the four oxygens. Thus part of the 5 additional pairs will be inter-atomic O-O pairs which contribute much less to the electron repulsion energy. Because the magnitude of the on-site electron repulsion integrals is about the same for Mn and O, it is more profitable to add the extra electron to the oxygens than to the metal. (The increase in inter-atomic Mn-O pairs will be about the same if we add the extra electron to the metal or to the oxygens.) The same line of reasoning can be used to explain the fact that no charge transfer is observed upon a ligand \rightarrow metal "charge-transfer" excitation.

4. Conclusions

The analysis in this paper illustrates the possible anomalous behaviour of the HF wavefunction in multiply bonded systems with weak interactions. The total HF

bond energy is the sum of two contributions with different sign: a) an energy stabilizing or negative contribution due to the interaction of the two atoms and b) a destabilizing or positive contribution associated with the HF error. In optimizing the bond-energy a HF calculation will try to maximize a) and at the same time minimize b). The magnitudes of both contributions are determined by overlap, the interaction matrix element, electron repulsion integrals etc. and also by the degree of localization of the orbitals. In case of a strong interaction and a small HF error, which is the situation for most systems that are well described on HF level, the HF calculation will choose to maximize the energy lowering associated with the interaction. The orbitals will come out delocalized and the covalent character of the bonds will be correctly described. In case of weak interaction and a large HF error, however, it becomes important for the HF wavefunction to minimize the increase in electron repulsion energy, associated with the HF error. Well known examples of this situation are dissociating molecules where the interaction is very weak and becomes zero in the limit of complete dissociation. The HF function describing a singly bonded, weakly interacting system is often triplet unstable [8], i.e., the energy can be lowered by assigning different spins to different space orbitals (UHF method) and breaking the symmetry. In multiply bonded systems, the HF wavefunction can reduce the magnitude of the HF error by localizing the bonding orbitals (retaining, however, the closed shell character) giving the individual bonds too much ionic character. This kind of orbital localization is easily detected if it requires symmetry breaking, in which case the symmetry adapted HF function is singlet unstable [8]. However, it is important to note that the conditions that favour a large HF error and orbital localization are not symmetry dependent and may equally well occur in those systems in which there is no symmetry breaking to alert us.

Transition metal molecules represent a group in which all conditions that favour orbital localization are already present at equilibrium distance: weak interaction and small overlap due to Pauli repulsion, often multiple bonding involving $3d$ orbitals and relatively large $3d$ - $3d$ repulsion (due to the compact nature of the $3d$ orbitals). Almost all of these molecules are described only poorly at the SCF level (they are often unbound!), and many show unrealistic localization effects, with or without symmetry breaking. In this context, it is interesting to note that it has by now been extensively documented that Density Functional (DF) calculations are much more successful in describing metal-ligand bonding than Hartree-Fock calculations [12-18]. In particular, they do not exhibit the anomalous HF behaviour discussed in this paper. This can be explained by the fact that a "HF-like" weak-interaction error is absent in DF calculations. An extensive discussion of this point has been given by Cook and Karplus [19] and by Tschinke and Ziegler [20].

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