

Frontier Hybrid Orbitals. II. Applications

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In this paper, the frontier hybrid orbitals (FHO's) of a series of octahedral ML_5 fragments are used to discuss the electronic structure and the chemical bond of these fragments and the molecules built of these ML_5 fragments. The bond orbitals which are chosen as the linear combination of the frontier hybrid orbitals of fragments are calculated and explain the electronic structure and properties of molecules such as $Mn(CO)_5L$ ($L = H, CN, CH_3, Cl$), M_2L_{10} , and $XM_2L'_{10}$ built of ML_5 fragments. The bond orbitals of $Mn-Mn$ in $Mn_2(CO)_{10}$ and $[Mn_2Cl_{10}]^{-4}$ are studied on the basis of FHO. And the three center bond of $Cr-HCr$ in $[(CO)_5Cr-H-Cr(CO)_5]^-$ ion is also discussed. The $Cr-H-Cr$ bond is bent and the bond angles is found to be about 150° . Besides, Mn chemical shifts in $Mn(CO)_5L$ ($L = H, CN, CH_3, Cl$) complexes are compared with the overlap integrals between FHO of $Mn(CO)_5$ and L , showing that there is a consistent relationship between them.

INTRODUCTION

Qualitative methods of understanding molecular electronic structures are based either on the valence theory promoted largely by Linus Pauling¹ or delocalized molecular orbital theory following the philosophy suggested by Robert Mulliken. The orbital interaction model based upon delocalized molecular orbital theory, was largely pioneered by Robert Hoffmann and Kenichi Fukui²⁻⁵. This model is simple and useful. But chemists are more familiar with the valence bond. In our works, a model which combines the two viewpoints is proposed. A large molecule is analyzed by the valence bond among the hybrid orbitals of fragments or small molecules, of which the large molecule is composed, which is calculated on the delocalized molecular orbital theory.

In part I of these series, the name "Frontier Hybrid Orbitals (FHO)" was proposed to describe the directional, characteristic hybrid orbitals of a fragment. In this work, the FHO's of a series of octahedral ML fragments are calculated in terms of the calculation method described in the above paper, and applied to discuss the electronic structure and the chemical bond of these fragments and the molecules built of these fragments. The CNDO/2-UHF calculation method is applied, and the standard atomic CNDO/2 parameters and the detailed geometries of fragments are chosen as⁵.

OCTAHEDRAL ML_5 FRAGMENTS

The fragment orbitals of an ML_5 group are well-known³⁻⁴. When one ligand is removed from the octahedron ML_6 , which is a saturated (18-electron) d^6 complex, to a first approximation, the C_{4v} point group of the fragment ML_5 is formed⁶. Removal of the ligand loses one antibonding interaction between the metal and ligand orbital, then goes down in energy. The resultant orbital is hybridized out away from the remaining ligands, toward the missing ligand. This will be a general phenomena that we will find in the fragment orbitals.

An octahedral ML_5 fragment will be a highly directional orbital, which is illustrated in Figure 1. This highly directional orbital is the frontier hybrid

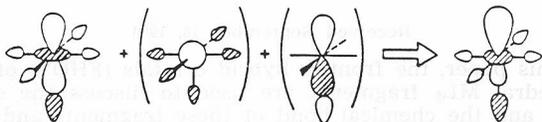


Figure 1. Typical FHO of $d ML_5$ fragment

orbital (FHO) of the fragment, which was described in part I of this series⁵. In a d^6 complex such as $Cr(CO)_5$, the FHO would be empty. $Cr(CO)_5$ itself has been experimentally studied by matrix isolation spectroscopy⁷. A square-pyramidal geometry was determined to be the ground state. An extensive series of ab initio molecular orbital calculations on the ground and number of excited electronic states in $Cr(CO)_5$ has been carried out⁸. The d^7 $Mn(CO)_5$ molecule where there is one electron in FHO has been investigated⁹⁻¹⁰. $Mn(CO)_5$ is isolobal to the methyl radical. This is the isolobal analogy proposed by Hoffman². And recently the interaction diagram of a pyridazine ligand with an ML_5 fragment in both monodentate and bidentate coordination modes has been presented by S. Alvarez¹¹.

According to the calculation method described in the above part of this series⁵, the FHO's of a series of octahedral ML_5 fragments are determined and listed in Tables I and II. The FHO's of d^7 ML_5 fragments are listed in Table I, and their contour diagrams are illustrated in Figure 2. From the point of Hoffmann's isolobal analogy, the d^7 ML_5 fragment is isolobal to methyl radical, that is,



TABLE I

FHO of a series of $d^7 ML_5$ fragments

Fragment	Coefficients of FHO			Fragment	Coefficients of FHO		
	4s	4p	3d		4s	4p	3d
$Mn(CO)_5$	0.198	0.446	0.873	$Mn(CN)_5^{5-}$	0.224	0.466	0.856
$Fe(CO)_5^+$	0.136	0.285	0.949	$Co(CN)_5^{3-}$	0.108	0.225	0.968
$Cr(CO)_5^-$	0.248	0.561	0.790	$Mn(PH_3)_5$	0.097	0.259	0.961
MnH_5^{5-}	0.482	0.831	0.263	$MnCl_5^{5-}$	0.844	0.510	0.167

TABLE II

Fragment	Multiplicity	Feature of FHO*	
Fe(CO) ₅	1	L	0.146(4s) + 0.302(4p _z) + 0.942(3d _{z²})
Cr(CO) ₅	1	E	0.214(4s) + 0.426(4p _z) + 0.879(3d _{z²})
V(CO) ₅	4	S	0.260(4s) + 0.617(4p _z) + 0.743(3d _{z²})
		S	dxz
		S	dyz
MnCl ₅ ²⁻	5	S	0.070(4s) + 0.133(4p _z) + 0.989(3d _{z²})
		S	dxz
		S	dyz
		S	dxy
Cr(CO) ₅ ⁺	2	S	dxy
Cr(CO) ₂ Cp	2	S	0.116(4s) + 0.407(4p _z) + 0.916(3d _{z²})
Cr(CO) ₂ Cp	4	S	0.158(4s) + 0.519(4p _z) + 0.840(3d _{z²})
		S	0.050(4s) + 0.234(4p _z) + 0.971(3d _{z²})
		S	0.009(4s) + 0.157(4p _z) + 0.988(3d _{z²})
[CrF ₅] ²⁻	1	E	0.211(4s) + 0.397(4p _z) + 0.893(3d _{z²})
[CrF ₅] ³⁻	2	S	0.707(3d _{xz}) + 0.707(3d _{yz})

* Note: Where symbols L, S, and E are used to represent the lone pair, single-electron, and empty hybrid orbitals, respectively.

Thus, the fragments listed in Table I are all isolobal to CH₃, and isolobal to each other. Table I shows that all FHO's are composed of 4s, 4p, and 3d, which is an analogy. The FHO's of these isolobal fragments are different in

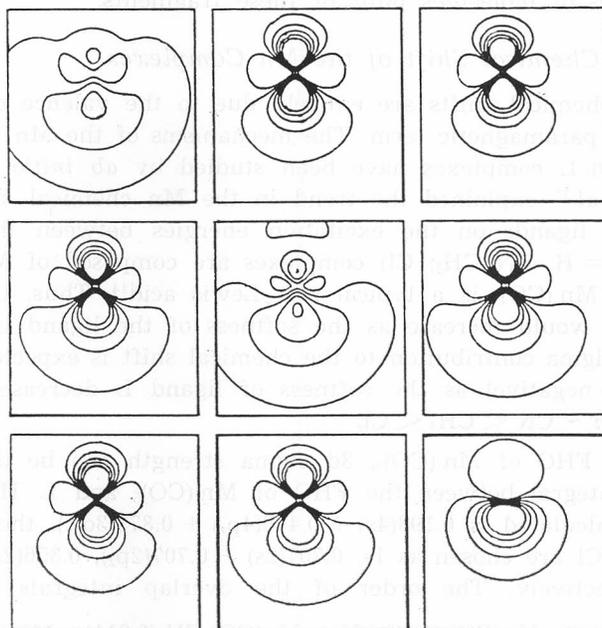


Figure 2. Contour diagrams of FHO's listed in Table I, CH₃ (a), Mn(CO)₅ (b), Fe(CO)₅⁺ (c), Cr(CO)₅ (d), MnH₅⁵⁻ (e), Mn(CN)₅⁵⁻ (f), Co(CN)₅³⁻ (g), Mn(PH₃)₅ (h), MnCl₅⁵⁻ (i). Contours shown are -0.04, 0.02, 0.08, 0.14, and 0.20.

quantity to varying degrees. This difference can be easily found from the contour diagrams of FHO's shown in Figure 2. In general, for a ML_5 fragment, the s composition of the FHO increases in the order $Cr > Mn > Fe > Co$, and the d composition increases in the opposite direction $Co > Fe > Mn > Cr$. When the ligand of an ML_5 fragment is substituted, the FHO will change in quantity. For example, the calculation results of $Mn(PH_3)_5$ and $MnCl_5^{5-}$ are very different so that it is difficult to say they are isolobal (see Table 1 and Figure 2).

In general, an ML_5 fragment is more reactive than the methyl radical. For a d^6 ML_5 fragment, its FHO is empty and can accept a generalized two-electron sigma donor ligand. For a d^7 ML_5 fragment, its FHO has one electron, and can form a sigma bond with another ligand or fragment with one electron in the FHO to resume the stable octahedral geometry.

On the other hand, some ML_5 fragments which have lone-pair or empty frontier hybrid orbitals, and have more than one single-electron, and have a Cp ($Cp^- = L_5$) ligand, have been also calculated. The results of their FHO's are listed in Table II. From Table II, the above discussions are consistent. In terms of the FHO results illustrated in Tables I and II, the molecules built of these fragments can be studied.

MOLECULES BUILT OF ML_5 FRAGMENTS

In this section, the FHO's of octahedral ML_5 fragments are used to discuss some properties of molecules built of these fragments.

1. The Metal Chemical Shift of the Mn Complexes

The Mn Chemical shifts are entirely due to the valence orbital contributions to the paramagnetic term. The mechanisms of the Mn chemical shift of the $Mn(CO)_5L$ complexes have been studied by *ab initio* calculations¹². Calderazzo *et al.*¹³ explained the trend in the Mn chemical shift from the effects of the ligands on the excitation energies between the d orbitals. $Mn(CO)_5L$ ($L = H, CN, CH_3, Cl$) complexes are composed of $Mn(CO)_5$ fragments and L. $Mn(CO)_5$ is a typical soft Lewis acid¹⁴. Thus, the interaction with ligand L would increase as the softness of the ligand base increases. Then, the 3d sigma contribution to the chemical shift is expected to increase (become more negative) as the softness of ligand L decreases, namely, in the order of $H \sim CN < CH_3 < Cl$.

Using the FHO of $Mn(CO)_5$, 3d sigma strength can be determined by the overlap integral between the FHO of $Mn(CO)_5$ and L. Here, the FHO of $Mn(CO)_5$ calculated is $0.198(4s) + 0.446(4p_z) + 0.873(3d_{z^2})$, the FHO's of H, CN, CH_3 , and Cl are chosen as $1s$, $0.707(2s) + 0.707(2p_z)$, $0.356(2s) + 0.935(2p_z)$, and $3p_z$ respectively. The order of the overlap integrals calculated is,

$$Mn(CO)_5H(0.482) > Mn(CO)_5CN(0.475) > Mn(CO)_5CH_3(0.311) > Mn(CO)_5Cl(0.302).$$

Figure 3. shows the consistent relationship between the overlap integrals and the experimental and calculated values¹² of Mn chemical shift.

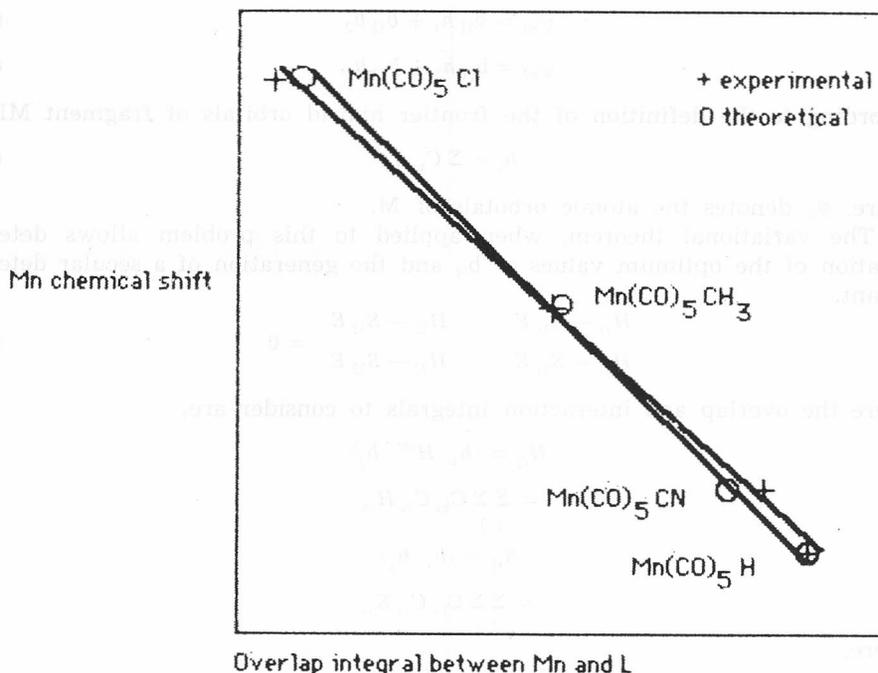


Figure 3. The relationship between Mn chemical shift and the sigma overlap integrals of Mn—L in $\text{Mn}(\text{CO})_5\text{L}$.

2. M_2L_{10} Molecules

Since CH_3 is isolobal with $\text{Mn}(\text{CO})_5$, one can replace one or both CH fragments in ethane to give $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$. These are well known molecules. Because of one single-electron in the FHO of this fragment, the electronic description of the three molecules is similar, that is there is a sigma bond present between C—C, C—Mn, or Mn—Mn. In general, the $d^7 \text{ML}_5$ fragment is isolobal with CH_3 . Thus two $d^7 \text{ML}_5$ fragments can be combined to form a M_2L_{10} molecule, which has a sigma bond between M—M. When the number of d electrons of M is not equal to 7, the ML_5 fragment does not resemble CH_3 . Then, the problem is whether the molecule M_2L_{10} exists. The answer is certain. For a $d^n \text{ML}_5$ fragment, when $n \leq 7$, the bond order of molecule M_2L_{10} built of the fragments is $8 - n$. For example, $d^7 \text{Re}_2(\text{CO})_{10}$ has a single sigma bond between the two metal atoms. In the case of a d^5 metal, a formal triple bond is predicated. Indeed, $\text{Cp}_2\text{M}_2(\text{CO})_4$ species (M = Cr, Mo, W), isoelectronic with the unknown $\text{V}_2(\text{CO})_{10}$ molecule, with this electron configuration have very short M—M distances, where Cp is equivalent to three coordinated ligands. The properties of ligand L also affect the bond between the two ML_5 fragments. We find that the HFO's of fragments and orbital interactions can determine the bond order, bond strength, and bond orbital levels between the M—M.

The bond orbitals between two ML_5 fragments symbolized by ψ_b , which are chosen as the linear combination of the frontier hybrid orbitals of fragments denoted by h_i , have the following form,

$$\psi_{b1} = b_{11} h_1 + b_{12} h_2 \quad (2)$$

$$\psi_{b2} = b_{21} h_1 + b_{22} h_2 \quad (3)$$

According to the definition of the frontier hybrid orbitals of fragment ML_5 ,

$$h_i = \sum C_{i\mu} \varphi_{\mu} \quad (4)$$

where, φ_{μ} denotes the atomic orbitals of M.

The variational theorem, when applied to this problem allows determination of the optimum values of b_{ij} and the generation of a secular determinant,

$$\begin{vmatrix} H_{11} - S_{11} E & H_{12} - S_{12} E \\ H_{21} - S_{21} E & H_{22} - S_{22} E \end{vmatrix} = 0 \quad (5)$$

where the overlap and interaction integrals to consider are,

$$\begin{aligned} H_{ij} &= \langle h_i | H^{\text{eff}} | h_j \rangle \\ &= \sum_i \sum_j C_{i\mu} C_{j\nu} H_{\mu\nu} \end{aligned} \quad (6)$$

$$\begin{aligned} S_{ij} &= \langle h_i | h_j \rangle \\ &= \sum_i \sum_j C_{i\mu} C_{j\nu} S_{\mu\nu} \end{aligned} \quad (7)$$

where,

$$H_{\mu\nu} = \langle \varphi_{\mu} | H^{\text{eff}} | \varphi_{\nu} \rangle \quad (8)$$

$$S_{\mu\nu} = \langle \varphi_{\mu} | \varphi_{\nu} \rangle \quad (9)$$

Equation (5) may be written in a shorthand way as,

$$| H_{ij} - S_{ij} E | = 0 \quad (10)$$

By solving this secular equation, the bond orbital energy levels between the two fragments in a molecule can be derived.

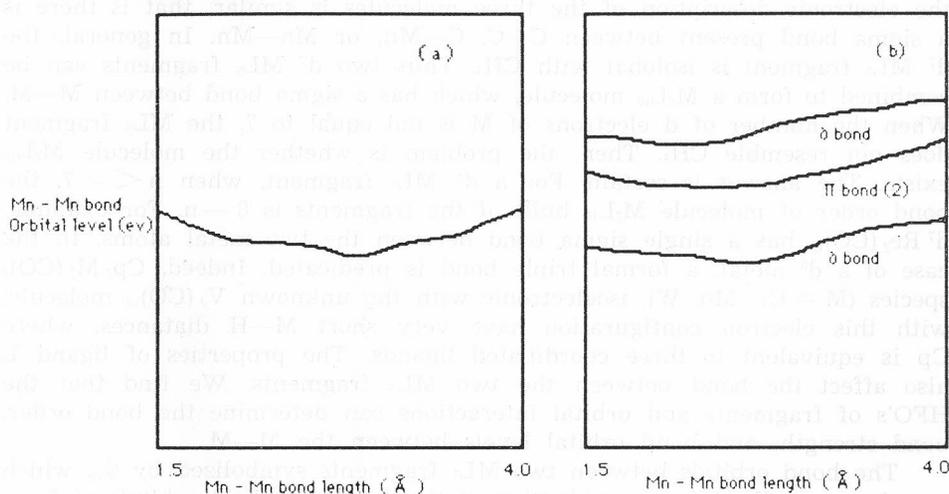


Figure 4. Mn—Mn bond orbital levels diagram of $Mn_2(CO)_{10}$ (a), and $[Mn_2Cl_{10}]^{4-}$ (b).

Using this method, we study the Mn—Mn bonds of $\text{Mn}_2(\text{CO})_{10}$, and $\text{Mn}_2\text{Cl}_{10}^{4-}$, and compare the differences between them. The bond orbital

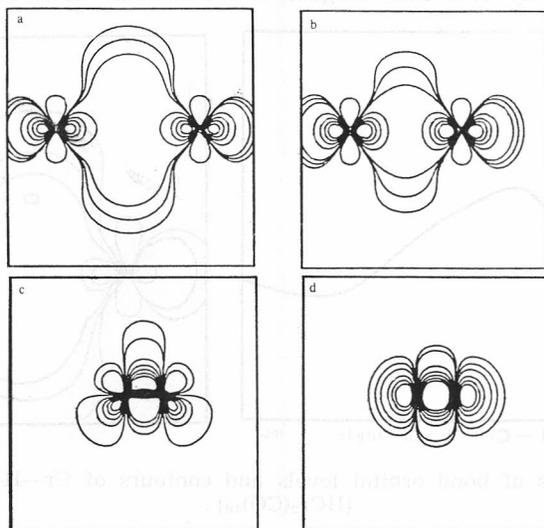


Figure 5. Contour diagrams of Mn—Mn bond orbitals for $\text{Mn}_2(\text{CO})_{10}$ (a), $[\text{Mn}_2\text{Cl}_{10}]^{4-}$ (b, σ bond; c, n bond; d, δ bond.)

levels are diagrammed with the changes of the Mn—Mn distances (see Figure 4). From Figure 4, it can be seen that the Mn—Mn distance in $\text{Mn}_2(\text{CO})_{10}$ of about 3.10 Å is much longer than the corresponding distance (2.40 Å) in $\text{Mn}_2\text{Cl}_{10}^{4-}$, which shows that the metal-metal interactions are larger in halide because CO is a typical pi acceptor ligand, Cl is a typical pi donor. This bond orbital model does not involve the repulsions between groups and other atoms, so the calculation results of bond orbitals need to be modified. But it is consistent with the experimental values of bond length¹⁵ qualitatively. The contours of bond orbitals of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2\text{Cl}_{10}^{4-}$ are illustrated in Figure 5.

3. XM_2L_{10} Molecules

XM_2L_{10} is an other type of simple molecules built of ML_5 fragments. The typical molecules are $[(\text{CO})_5\text{Cr—H—Cr}(\text{CO})_5]^-$, $\text{Cp}(\text{CO})_2\text{Cr—SCr}(\text{CO})_2\text{Cp}$, and $[\text{F}_5'\text{Cr(II)—F—Cr(III)F}_5]^{6-}$. The isoelectronic molecule with $\text{SCr}_2(\text{CO})_4\text{Cp}_2$ is $[(\text{CO})_5\text{Cr—S—Cr}(\text{CO})_5]^{2+}$. The good pi contribution to the Cr—S linkages suggests the description $\text{Cp}(\text{CO})_5\text{C}=\text{S}=\text{Cr}(\text{CO})_5\text{Cp}^{2+}$ for this molecule. Sometimes, in these units the M—X—M in XM_2L_{10} bridge is linear, otherwise it is bent, the distortion of the symmetric structure to an asymmetric one. In $\text{HCr}_2(\text{COO})_{10}^-$ ions, the hydrogen atom lies off the Mn—Mn axis¹⁶. Asymmetric structure appears in the Cr(II)/Cr(III) mixed valence species. The inner sphere redox behavior of the Cr(II)/Cr(III) system has been studied in great detail¹⁷.

In this work, the bond orbitals of M—X—M in XM_2L_{10} complex may be derived in a similar way by adding the hydrogen 1s orbital to the bond orbital produced by two ML_5 fragments set at the metal-metal distance in

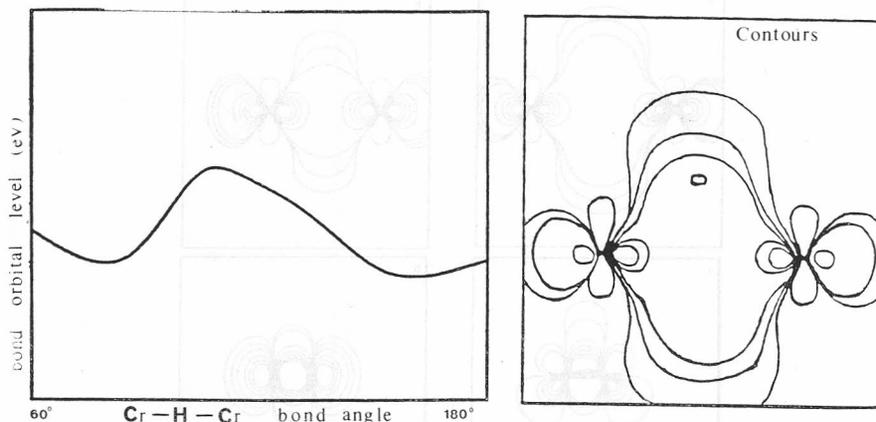


Figure 6. Plots of bond orbital levels and contours of Cr—H—Cr bond in $[HCr_2(CO)_{10}]^-$.

a molecule of this type, as mentioned above. The $[(CO)_5Cr-H-Cr(CO)_5]^-$ ion is considered to be composed of two $Cr(CO)_5^-$ fragments with one single-electron in each FHO, and hydrogen 1s orbital which is empty. Thus, the Cr—H—Cr bond is considered as a two-electron three-center bond, the bond orbital is the linear combination of FHO's of $Cr(CO)_5^-$ and H^+ . Using this method, we calculate the bond orbital levels in $[(CO)_5Cr-H-Cr(CO)_5]^-$ ion. The results are diagrammed in Figure 6. In terms of the result (see Figure 6), it follows that the Cr—H—Cr bond is not linear but bent. The Cr—H—Cr bond angles is found to be about 150° for the most stable structure. Figure 6 shows the bond orbital levels as the Cr—H—Cr angle changes from 180° to 30° . What happens is that the overlap integral between Cr_1 and Cr_2 is switched on. This stabilizes the bond orbital since Cr_1 and Cr_2 enter with the same relative phase both of these hybrid orbitals. During the bending process, these orbitals mix together to stabilize the Cr—H—Cr bond. But, due to repulsions between the fragments, the bent angle is limited.

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SAŽETAK

Granične hibridne orbitale. II. Primjene

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Granične hibridne orbitale primijenjene su na ispitivanje elektronske strukture i svojstva kompleksa izgrađenih od oktaedarskih fragmenata ML_5 tipa.