

Frontier Hybrid Orbitals. I. Principles*

Cao Yang and Wang Youliang

Department of Chemistry, Suzhou University, Suzhou, People's Republic of China

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The purpose of the present paper is to describe a method, in quantitative sense, of discussing the isolobal analogy of fragments (or molecules) proposed by Hoffmann. The »Frontier Hybrid Orbitals (FHO)« are used to represent the directional, frontier orbitals of the central atom, which have the same meaning as the »lobes« involved in the concept of isolobal analogy. The calculation of Frontier Hybrid Orbitals (FHO's) is based on the natural hybrid orbitals which are the eigenvectors of density matrix blocks. The overlap integrals, bonding capabilities, and valence orbital energy levels of the FHO's of fragments are also calculated. The relationship between FHO and the isolobal analogy is discussed in this paper.

INTRODUCTION

The concept of the isolobal analogy was proposed by Hoffmann,¹⁻⁷ according to the Extended Huckel Molecular Orbital (EHMO) study results of molecular fragments, and the relationship between the hybrid orbitals of the valency bond picture introduced into chemistry by Pauling⁸ and the molecular geometry. Two fragments are said to be isolobal if the number, symmetry properties, approximate energy and the shape of the frontier orbitals and the number of their electrons are similar. From this point of view, the isolobal analogy is determined by the properties of the frontier orbitals of fragments or molecules. The utility of the isolobal analogy is that if two fragments are isolobal, then they should have a very similar electronic description, structural characteristic and reactivity in qualitative sense.

In the present paper we describe a way of discussing the isolobal analogy of molecular fragments depending on the atomic hybrid orbitals in quantitative sense. The »lobe« involved in the isolobal analogy is a strongly directional orbital forming a chemical bond, which is the delocalized frontier orbital and indicates the characteristic of electronic structure, bonding and reactivity of the fragment or molecule. The orbital, which has maximum bonding ability and is directional, can be substituted by the hybrid orbital of the central atom which is the localized result of molecular orbitals. We propose that the name »Frontier Hybrid Orbital (FHO)« be

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used for the orbital. In this work, the calculation method of FHO, the overlap integrals, bonding capabilities, and valence orbital energy level of FHO are described. And the relationship between FHO and isolobal analogy is primarily discussed.

CALCULATION METHOD

(1) Natural Hybrid Orbitals

For the closed-shell system, the LCAO MO's are of the form:

$$\Psi_1 = \sum_{\mu} C_{\mu 1} \Phi_{\mu} \quad (1)$$

In numerical applications, orthogonalized AO's are consistently used, *i. e.*

$$\int \Phi_{\mu} \Phi_{\nu} d\tau = \delta_{\mu\nu} \quad (2)$$

Now by definition,

$$P_{\mu\nu} = \sum_i n_i C_{\mu i}^* C_{\nu i} \quad (3)$$

$$P_{\mu\mu} = \sum_i n_i C_{\mu i}^2 \quad (4)$$

The matrix \mathbf{P} with the elements $P_{\mu\nu}$ or $P_{\mu\mu}$ is called the molecular density matrix. Consider the $n \times n$ density matrix \mathbf{P} as divided into atomic and inter-atomic blocks as,

$$\mathbf{P} = \begin{bmatrix} P_{AA} & P_{AB} & \dots & P_{AL} \\ P_{BA} & P_{BB} & \dots & P_{BL} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ P_{LA} & P_{LB} & \dots & P_{LL} \end{bmatrix} \quad (5)$$

here the submatrix P_{AA} of order $m \times m$ is associated with the m atomic orbitals on A. The nn transformation matrix is \mathbf{T} , the new matrix \mathbf{P}' is then given by

$$\mathbf{P}' = \mathbf{T} \mathbf{P} \mathbf{T} \quad (6)$$

Now suppose we make an orthogonal transformation of the atomic basis orbitals $\{\Phi\}$ into a new set $\{h\}$ such that the intraatomic off-diagonal elements of the new density matrix \mathbf{P}' are zero. The set $\{h\}$, originally proposed by McWeeny⁹, are called the natural hybrid orbitals (NHO). The transformation which converts the AO basis to the NHO basis is simply a special case of the general transformation \mathbf{T} , leading to the diagonalization of block \mathbf{P} and thus to the NHO's of A.

The transformation considered here is similar to that of the well-known Jacobi matrix diagonalization procedure.

$$P_{AA} h_1^{(A)} = n_1^{(A)} h_1^{(A)} \quad (7)$$

Where, $n_1^{(A)}$ and $h_1^{(A)}$ represent the eigenvalues and vectors, respectively. The eigenvectors are called the natural hybrid orbitals (NHO) of atom A.

(2) Frontier Hybrid Orbitals

For the open-shell system, the LCAO-MO's are of the form:

$$\Psi_i^\alpha = \sum_{\mu} C_{\mu i}^\alpha \Phi_{\mu} \quad (8)$$

$$\Psi_i^\beta = \sum_{\mu} C_{\mu i}^\beta \Phi_{\mu} \quad (9)$$

Now by definition,

$$P_{\mu\nu}^\alpha = \sum_i n_i C_{\mu i}^\alpha C_{\nu i}^\alpha \quad (10)$$

$$P_{\mu\nu}^\beta = \sum_i n_i C_{\mu i}^\beta C_{\nu i}^\beta \quad (11)$$

The total density matrix elements $P_{\mu\nu}$ are their sum,

$$P_{\mu\nu} = P_{\mu\nu}^\alpha + P_{\mu\nu}^\beta \quad (12)$$

But the spin density matrix elements $P_{\mu\nu}^s$ are defined as the subtraction of $P_{\mu\nu}^\beta$ from $P_{\mu\nu}^\alpha$,

$$P_{\mu\nu}^s = P_{\mu\nu}^\alpha - P_{\mu\nu}^\beta \quad (13)$$

Here, P^s and P_{AA}^s are used to denote the total spin density matrix and the block which only involves the atomic orbitals of atom A, respectively. In the diagonalization procedure as mentioned above,

$$P_{AA}^s h_i^{(A)} = n_i^{(A)} h_i^{(A)} \quad (14)$$

where, $n_i^{(A)}$ and $h_i^{(A)}$ represent the eigenvalues and vectors, respectively, on which the natural hybrid orbitals occupied by one-electron can be determined. According to Foster and Weinhold,¹⁰ the eigenvalues of molecular density matrix indicate the characteristic of the bond and the electronic structure of atoms in the molecule. For a fragment, which has one or more single-electrons, its spin density matrix can be obtained by molecular orbital calculation, and its natural hybrid orbitals occupied by single-electron can be determined by eq. (14). In general, when $n_i^{(A)} = 1$, the relative eigenvector $h_i^{(A)}$ is the natural hybrid orbital occupied by single-electron, for which we propose that the name »Frontier Hybrid Orbital« be used. For a fragment, which has no single-electron, but has empty orbitals or lone-pairs, its density matrix can be obtained by MO calculation, and its NHO's occupied by empty orbitals or lone-pairs can be determined by eq. (7). In general, when $n_i^{(A)} = 0$, the relative eigenvector $h_i^{(A)}$ is the lone-pair hybrid orbital. For these empty and lone-pair hybrid orbitals, we also propose that the name »Frontier Hybrid Orbitals« be used. It must be noted that the above discussion and conclusions are based on the fragments MO calculations of atomic valence orbitals and valence electrons.

Since the density matrix contains pertinent information about the system and can be defined in *ab initio* as well as semiempirical MO methods, the quantitative features of the definition do not depend on a particular MO approximation. Depending on the accuracy of the density matrix, which in turn depends on the wavefunction used, quantitative changes may occur for the value of Frontier hybrid orbitals.

(3) *Overlap Integrals, Bonding Capabilities, and Valence Orbital Energy Levels of Frontier Hybrid Orbitals*

The frontier hybrid orbitals (FHO's) of a fragment are a linear combination of the valence orbitals of the central atom, whose exponents are chosen as the orbital exponents of the central atom. To calculate the overlap integral between a FHO and another atomic orbital or another FHO, the overlap integral between the atomic orbitals of which the FHO is composed and other atomic orbitals is to be calculated first. Let h_k denote the FHO,

$$h_k = \sum_i C_{ik} \Phi_i \quad (15)$$

where Φ_i is the atomic orbitals of which the FHO is composed, so the overlap integral between h_k and Φ_j is,

$$S_{kj} = \langle h_k | \Phi_j \rangle = \sum_i C_{ik} S_{ij} \quad (16)$$

Symbol i indicates that the sum includes all atomic orbitals of which h_k is, composed. Then the overlap integral between h_k and other FHO which is denoted by h_l is,

$$S_{kl} = \langle h_k | h_l \rangle = \sum_i \sum_j C_{ik} C_{jl} S_{ij} \quad (17)$$

Here, symbol i has the same meaning as mentioned above, and symbol j indicates that the sum includes all atomic orbitals of which h_l is composed.

According to Mulliken,¹¹⁻¹² the bonding capability of a hybrid orbital can be determined by the overlap integrals between the hybrid orbital and the orbitals of another ligand. Based on the discussion of the bonding capabilities of fragments made by Hoffmann,² we suggest that the overlap integrals of FHO's of fragments with the atomic orbital of H atom be used as the relative bonding capabilities of the FHO's of fragments, represented by F . In general, for an organic fragment AL_n , the value of F is calculated when the distance of A—H is 1.10 Å. And for an inorganic fragment ML_n , the value of F is calculated when the distance of M—H is 1.50 Å.

The Valence Orbital Energy Level (VOEL) of a FHO is chosen as the weighted average of the energy levels of atomic orbitals of which the FHO is composed. For example, the FHO of CH is 0.354(s), 0.935(p), then its VOEL is,

$$\text{VOEL}(\text{CH}_3) = 0.354 \text{ VOEL}(\text{C}_s) + 0.935 \text{ VOEL}(\text{C}_p) = -0.757$$

The atomic valence orbital energy level values which are dealt with in this paper are listed in Table I, on the basis of CNDO/2 approximation.

TABLE I
Atomic VOEL values of CNDO/2 (eV)

Atom	ns	np	Atom	ns	np	(n-1)d
H	-0.38887		Cr	-0.0585	-0.0757	-0.798
B	-0.5887	-0.2253	Mn	-0.0537	-0.0709	-0.817
C	-0.8116	-0.4999	Fe	-0.140	-0.035	-0.943
N	-1.773	-1.330	Co	-0.494	-0.317	-1.716
Al	-0.451	-0.166	Ni	-0.875	-0.695	-2.573
Si	-0.579	-0.362	Cu	-1.189	-1.002	-3.083

RESULTS AND DISCUSSION

In this work, the CNDO/2-UHF method is applied to calculating a series of organic and inorganic fragments, whose geometrical details chosen are the same as Hoffmann's,^{2,5-7} and the standard CNDO/2 atom parameters are used. In terms of the calculation method mentioned above, the FHO's of these fragments are calculated and illustrated in Tables II and III. The

TABLE II
FHO's of some AH_3 fragments and their properties

Fragment	Feature*	Coefficients of atomic orbitals in FHO		F	VOEL
		s	p		
CH ₃	S	0.354	0.935	0.432	-0.757
CH ₃ ⁺	E	0.175	0.985	0.392	-0.635
CH ₃ ⁻	L	0.579	0.815	0.461	-0.878
BH ₃	E	0.243	0.970	0.519	-0.362
BH ₃ [*]	S	0.417	0.909	0.558	-0.451
BH ₃ ²⁻	L	0.571	0.821	0.579	-0.522
NH ₃	L	0.612	0.791	0.361	-2.137
NH ₃ ⁺	S	0.278	0.961	0.320	-1.771
NH ₃ ²⁺	E	0.116	0.993	0.287	-1.526
SiH ₃	S	0.403	0.915	0.601	-0.565
SiH ₃ ⁺	E	0.218	0.976	0.555	-0.480
SiH ₃ ⁻	L	0.558	0.830	0.624	-0.624

* Note: The empty, single-electron, and lone-pair hybrid orbitals are symbolized by E, S, and L, respectively.

TABLE III
FHO's of fragments shown in Figure 1 and their properties

Fragment	Symmetry	Coefficients of atomic orbitals in the FHO			F	VOEL	
		s	p	d			
CH ₃	C _{3v}	0.354	0.935		0.432	-0.755	
CH ₂	C _{2v}	0.508	0.861		0.454	-0.843	
CH	linear	0.646	1.000		0.342	-0.500	
			0.441		0.354	-0.745	
			1.000		0.342	-0.500	
Mn(CO) ₅	C _{4v}	0.198	1.000	0.573	0.435	-0.511	
			0.446	0.571	0.673	-0.629	
			0.665	0.959	0.307	-0.914	
Fe(CO) ₄	C _{3v}	0.481	0.284		0.717	-0.557	
			0.779	0.979	0.253	-1.745	
			0.204	0.979	0.253	-1.745	
CpFe(CO) ₂		0.104	0.204	0.979	0.253	-1.745	
			0.298	0.949	0.360	-0.920	
			0.354	0.391	0.850	0.497	-1.757
CpCo(CO)		0.108	0.413	0.904	0.408	-1.736	
			0.803	0.593	0.057	0.702	-1.261
			0.141	0.990	0.204	-2.645	
CpNi		0.073	0.140	0.987	0.236	-2.701	
			0.273	0.412	0.865	0.475	-1.750
			0.693	0.720	0.046	0.722	-1.225
Co(CO) ₃	C _{2v}	0.693	0.172	0.985	0.221	-2.654	
			0.602	0.126	0.707	-1.930	
			1.000		0.562	-1.000	
Ni(CO) ₂	C _{2v}	0.789	0.162	0.987	0.188	-3.241	
			0.602	0.126	0.707	-1.930	
			1.000		0.562	-1.000	
Cu(CO)	linear	0.789	0.162	0.987	0.188	-3.241	
			0.602	0.126	0.707	-1.930	
			1.000		0.562	-1.000	

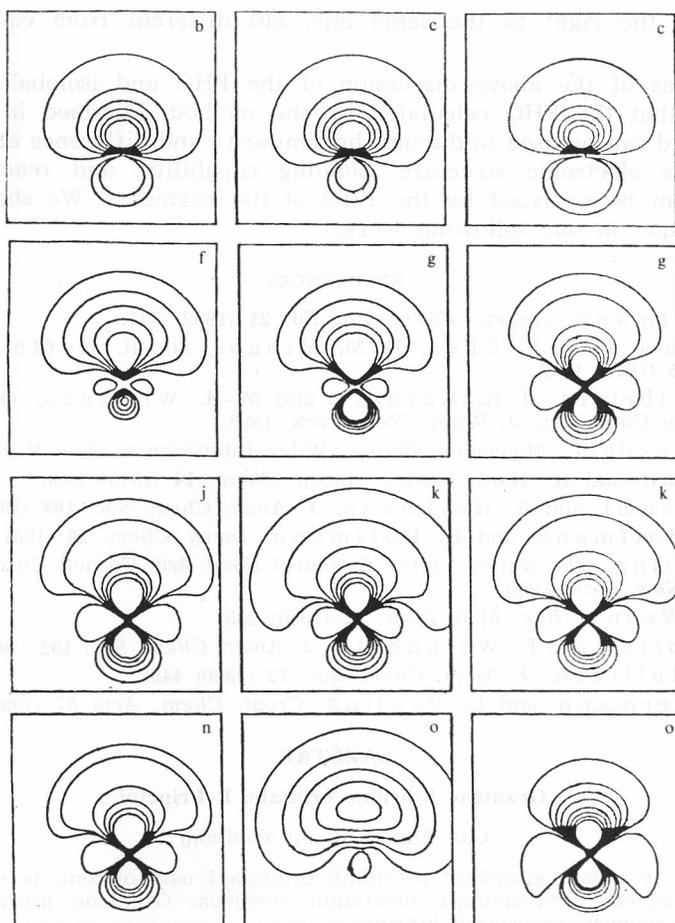


Figure 2. Contour diagrams of FHO's of fragments in Figure 1. Contours shown are: -0.04 , 0.02 , 0.08 , 0.14 , 0.20 , and 0.26 .

methyl radical, *b*. It has one FHO pointed in the direction of the missing hydrogen atom with one electron in it. Removal of another hydrogen atom generates methylene, *c*. There are two FHO's pointed to the two missing hydrogen atoms. Removal of still another hydrogen atom creates a methine fragment, *d*. It has three FHO's with three electrons partitioned between them. Now breaking one Cr—L bond from octahedral complex CrL_6 creates a CrL_5^- fragment, the neutral isoelectronic fragment of which is MnL_5 , *f*. It has one FHO directed toward the missing ligand with one electron in it. Removal of a second ligand from MnL_5 and moving one element to the right in the periodic table forms the FeL_4 fragment, *g*. And removal of a third ligand generates the CoL_3 fragment, *h*.

The FHO's of fragments shown in Figure 1 and their properties are illustrated in Table III. The contour diagrams of FHO's of fragments (*b*, *c*, *f*, *g*, *j*, *k*, *n*, *o*) are shown in Figure 2. From Table III and Figure 2, it can be seen that the FHO's of the fragments shown in Figure 1 are similar from

the left to the right in the same line, but different from each other in quantity.

In terms of the above discussion of the FHO and isolobal analogy, it is certain that the FHO calculated by the method described in this paper is useful and can be used to discuss the similarity and difference of fragments, so that the electronic structure, bonding capability, and reactivity of a molecule can be analyzed by the FHO of its fragments. We shall continue this discussion in our following work.

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SAŽETAK

Granične hibridne orbitale. I. Principi

Cao Yang i Wang Youliang

Uveden je pojam graničnih hibridnih orbitala i ustanovljena je njihova relacija s konceptom ekvivalentnih orbitalnih reznjeva. Granične hibridne orbitale dobivene su pomoću »prirodnih hibrida«.