

# Density Localization of Atomic and Molecular Orbitals

## III. Heteronuclear Diatomic and Polyatomic Molecules

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Density localized molecular orbitals are computed for the molecules LiH, LiF, BF, BN, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and HF. The density localization method is based on the minimization of the sum of the interorbital density overlap integrals. The results of this method are compared to the results of the energy localization method of Edmiston and Ruedenberg and the localization procedures of Boys and of Magnasco and Perico. The agreement among the results obtained by these four methods is in general good. With a few exceptions the localized molecular orbitals agree with the classical chemical concepts.

Dichtelokalisierte Molekülorbitale sind berechnet worden für die Moleküle LiH, LiF, BF, BN, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O und HF. Die Dichtelokalisierungsmethode beruht auf der Minimierung der Summe der Dichteüberlappungsintegrale zwischen verschiedenen Orbitalen. Die Ergebnisse dieses Verfahrens werden verglichen mit den Resultaten der Energielokalisierungsmethode von Edmiston und Ruedenberg und den Verfahren von Boys und von Magnasco und Perico. Die Übereinstimmung zwischen den verschiedenen Methoden ist im allgemeinen gut. Mit einigen Ausnahmen werden die klassischen chemischen Vorstellungen von Elektronenpaaren reproduziert.

### 1. Introduction

In a previous paper [1] (we refer to it as I) we have given the general theory of the density localization method. In a subsequent work [2] (we refer to it as II) we have applied this method to the homonuclear diatomic molecules Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, and F<sub>2</sub> and have compared the results with those of the energy localization method of Edmiston and Ruedenberg [3, 4] and the localization procedures of Boys [5, 6] and of Magnasco and Perico [7]. In the present paper we apply these four methods to the molecules LiH, LiF, BF, BN, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and HF. We find – as in II – that the calculated localized molecular orbitals (LMO's) agree in general with the classical chemical concepts of inner shells, lone pairs of electrons and bonds which are used to describe the electronic structure of molecules. Exceptions are the molecules LiF, BN, and CO. However, just these exceptions offer additional insight into the concept of localized orbitals. The numerical agreement among the results of the four methods is in most cases quite satisfactory. For a few molecules – in particular those involving lone pairs of electrons – the results of the Magnasco-Perico method exhibit greater deviations from the general agreement, but it does not seem possible to establish a general trend. After describing briefly the four localization methods under investigation in Sect. 2 we discuss the calculations in detail in Sect. 3. In Sect. 4 we analyze the atomic hybrids for all molecules examined so far.

## 2. Short Outline of the Four Localization Methods

We present only a short outline of the general idea of the energy, density, Boys, and Magnasco-Perico localization methods. For all details we refer to the original papers [1–7] and to review articles [8–10]. The considerations will be restricted to closed shell cases, where the wavefunction is approximated by a single Slater determinant. The doubly filled orthonormal real orbitals are determined by a SCF calculation. For the wavefunction of a system with  $2n$  electrons we write

$$|\Psi\rangle = (2n!)^{1/2} \mathcal{A}\{|1+\rangle|1-\rangle\cdots|n+\rangle|n-\rangle\}. \quad (1)$$

where  $\mathcal{A}$  is the antisymmetric projection operator with  $\mathcal{A}^2 = \mathcal{A}$ . Let  $|\Phi\rangle$  denote the row vector of molecular orbitals (MO's).

$$|\Phi\rangle = (|1\rangle, \dots, |i\rangle, \dots, |n\rangle). \quad (2)$$

Any unitary transformation, applied to  $|\Phi\rangle$  leaves the wavefunction  $|\Psi\rangle$  invariant. This can be used to transform the canonical molecular orbitals (CMO's) to the LMO's. Such a unitary transformation is common to all the localization methods under investigation, they only differ by the choice of a functional which is to be extremized by the transformation. This functional will be called localization function and is chosen by physical arguments.

They energy localized molecular orbitals (ELMO's) of Edmiston and Ruedenberg [3, 4] are obtained by maximizing the sum of the orbital self-interaction energies

$$D = \sum_i [ii|ii]. \quad (3)$$

Because of the separate invariance of the total Coulomb and total exchange interaction energy this is equivalent to minimizing separately the sum of the interorbital exchange energies and the sum of the interorbital Coulomb energies.

The density localized molecular orbitals (DLMO's) are defined to be those orbitals resulting from the unitary transformation which minimizes the sum of the interorbital density overlap integrals [1]

$$D = \sum_{i < j} [i^2 j^2]. \quad (4)$$

The density overlap between the MO's is given by

$$[i^2 j^2] = \int |\langle \mathbf{r} | i \rangle|^2 |\langle \mathbf{r} | j \rangle|^2 d^3 \mathbf{r}, \quad (5)$$

where  $|\langle \mathbf{r} | i \rangle|^2$  is the charge density of orbital  $|i\rangle$ .

The localized molecular orbitals of Boys (BLMO's) are determined by minimizing the sum of the quadratic repulsions of the orbitals with themselves [5, 6]:

$$I = \sum_i \langle ii | r_{12}^2 | ii \rangle. \quad (6)$$

This has been shown by Boys to be equivalent to a maximization of the sum of the squares of the distances between the orbital charge centroids:

$$D = \sum_{i,j} [\langle i | \mathbf{r} | i \rangle - \langle j | \mathbf{r} | j \rangle]^2. \quad (7)$$

The latter formula is more appropriate for numerical implementation.

The localization procedure of Magnasco and Perico [7] is an external method [11], i.e. a concept of the orbital structure is required prior to localization. The starting point is the definition of local electron populations for each MO, which have to be localized around atoms or between pairs of atoms. The localization function in this case is the sum of these local populations:

$$P = \sum_i P_i, \quad (8)$$

where

$$P_i = \sum_{p,q \in \Gamma_i} C_{pi} C_{qi} \langle p|q \rangle \quad (9)$$

and where  $\Gamma_i$  denotes the set of functions making up this population. Maximization of  $P$  defines the uniformly localized molecular orbitals of Magnasco and Perico (MPLMO's).

The actual process of localization is done via a sequence of pairwise rotations of the MO's which are chosen to extremize the localization function.

### 3. The Calculations

Localized molecular orbitals have been computed using the formalism described above for the molecules LiH, LiF, BF, BN, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, and HF. The calculations are based on SCF wavefunctions obtained with a program written by the author. The MO's are expanded in a set of Gaussian lobe functions. As basis set we used: at the H atom 4 *s*-type functions, the two functions with the largest exponents contracted into one group, at the Li atom 9 *s*-type functions, the five functions with the largest exponents contracted into one group, and 2 *p*-type functions, and at the atoms B to F 9 *s*-type functions, the five functions with the largest exponents contracted into one group, and 5 *p*-type functions, the three functions with the largest exponents contracted into one group. The exponential parameters and contraction coefficients of the *s*-type functions are taken from Huzinaga's paper [12], of the *p*-type functions (atoms B to F) from Whitten's paper [13]. For the Li atom the exponents  $\eta$  of the *p*-type functions and the distance  $R$  from the center are:  $\eta_1 = 0.5$ ,  $R_1 = \pm 0.075$  a.u.,  $\eta_2 = 2.0$ ,  $R_2 = \pm 0.065$  a.u. Table 1 contains information about the geometry of the molecules used in the calculations and about the total energies computed.

The LMO's which we have obtained agree for most of the molecules with the results of Edmiston and Ruedenberg [4, 14] and other authors [15, 16], wherever a comparison is possible, except for the molecules LiF, BF, and CO. We are going to discuss these results in detail below.

Before examining in detail the individual molecules we make a few general statements about the numerical results. We find again – as has been found in II – that the numerical agreement among the results of the four localization methods is in general quite satisfactory, the best agreement being found among the results of the three intrinsic methods, where differences of about 1% in the value of the more "important" coefficients ( $c \geq 0.1$ ) are typical. For some of the molecules the MPLMO's show greater differences. Whereas the results of all four localization

Table 1. Geometries and total energies

Molecule	Geometrical parameters <sup>a</sup>	<i>E</i> [a.u.]
LiH	R = 3.01483	- 7.978159
LiF	R = 2.8535	- 106.953533
BF	R = 2.3849	- 124.100587
BN	R = 2.4208	- 78.868576
CO	R = 2.132	- 112.693805
C <sub>2</sub> H <sub>2</sub>	R <sub>CH</sub> = 2.0101, R <sub>CC</sub> = 2.2696	- 76.807095
CH <sub>4</sub>	R <sub>CH</sub> = 2.0617	- 40.183581
NH <sub>3</sub>	R <sub>NH</sub> = 1.9162 HNH = 106.8°	- 56.174877
H <sub>2</sub> O	R <sub>OH</sub> = 1.663 HOH = 104.5°	- 75.993520
HF	R = 1.7328	- 100.019503

<sup>a</sup> distances are given in atomic units.

Table 2. 2*p*-type populations of unnormalized hybrids on different atoms in bond and lone pair LMO's

Atom	Bond orbital				Lone pair orbital			
	ELMO	DLMO	BLMO	MPLMO	ELMO	DLMO	BLMO	MPLMO
B in B <sub>2</sub>	0.1973	0.2045	0.1904	0.2492	0.2067	0.2006	0.2122	0.1673
N in N <sub>2</sub>	0.3046	0.3119	0.2997	0.3362	0.2618	0.2417	0.2735	0.1883
F in F <sub>2</sub>	0.3768	0.3909	0.3452	0.3695	0.6888	0.6847	0.6956	0.6904
F in LiF	0.7039	0.7000	0.7008	0.5701	0.7413	0.7407	0.7426	0.7842
B in BF	0.0525	0.0600	0.0477	0.0457	0.1118	0.1039	0.1170	0.1188
F in BF	0.5735	0.5753	0.5828	0.6074	0.6756	0.6768	0.6714	0.6571
N in BN	0.3863	0.3359	0.4087	0.4328	0.2245	0.3533	0.1601	0.0619
C in CO	0.1259	0.1371	0.1223	0.1387	0.1765	0.1615	0.1928	0.1722
O in CO	0.5091	0.3912	0.5130	0.5834	0.4007	0.5142	0.3823	0.1749
N in NH <sub>3</sub>	0.3303	0.3316	0.3280	0.2999	0.7026	0.6982	0.7095	0.7912
O in H <sub>2</sub> O	0.3929	0.3954	0.3884	0.3497	0.7005	0.6979	0.7051	0.7423
F in HF	0.4799	0.4803	0.4712	0.4973	0.7162	0.7162	0.7197	0.7109

methods agree well in the structure of the inner shell orbitals the agreement for the lone pair and bond orbitals is sometimes less good. The MPLMO's show the greatest differences from the ELMO's in molecules with lone pair orbitals, except for the HF molecule where the agreement is very good. It appears difficult to establish general trends; in addition a dependence of the results on the basis set size seems probable.

For the inner shell orbitals we find the strongest participation of the Gaussian basis functions with the smallest exponents in the MPLMO's, the contribution decreasing for the DLMO's, ELMO's, and BLMO's in the given order. For molecules containing lone pairs of electrons it is stated in the literature that the MPLMO's have a greater local 2*p*-type population in the localized lone pair orbitals than do the ELMO's and that the reverse is true for the bond orbitals [7, 17]. In II we have already commented on this feature.

Analyzing the localized orbitals for a fairly large number of molecules we cannot confirm the above statement. Table 2 contains the local 2*p*-type populations

in the lone pair and bond orbitals for several atoms. For some molecules the quoted behaviour is found, for others not. The MPLMO's show the greatest differences, but no general trend seems to emerge.

We describe qualitatively the LMO's resulting from the four localization methods. The lengthy expansions of the orbitals in terms of the Gaussian basis functions will not be given because of limitation of space<sup>1</sup>, but we present the transformation matrices from CMO's to LMO's which appear to be the most useful result because of their approximate independency of the basis set choice [4]. (For the notation used see Ref. [4]). In order to compare the results of the different localization methods the transformation matrices resulting from the Magnasco-Perico localization method have been subjected to an additional unitary transformation, which mixes the orbitals of  $\sigma$ - and  $\pi$ -symmetry [7]. The signs of the orbitals are chosen in the following way: The largest coefficient of an  $s$ -type or of a  $2p\pi$ -type function is chosen to be positive for each orbital. If there are two or more coefficients of equal magnitude, the first one carries the positive sign. In cases of degeneracy or wavefunctions calculated with greatly differing basis sets this might not suffice, but the major uncertainties should be eliminated in this way.<sup>1</sup>

### LiH (Table 3)

The orbitals of LiH are changed insignificantly by a localization. One obtains an inner shell on the Li atom and a bond orbital which is strongly polarized towards the H atom. From the transformation matrices given in Table 3 we see that the transformation is closest to the identity for the Boys method, and has greater deviations from the identity for the energy, the density and the Magnasco-Perico method. The exchange integrals calculated with the LMO's are reduced by a factor of about four compared to the exchange integrals calculated with the CMO's, for the density overlap integrals the factor is about ten.

Table 3

TRANSFORMATION MATRICES FOR LIH			
ENERGY LOCALIZATION		BOYS LOCALIZATION	
	iLi	b $\sigma$ LiH	
1 $\sigma$	0.99768	0.06811	1 $\sigma$ 0.99954
2 $\sigma$	-0.06811	0.99768	2 $\sigma$ -0.03020
			0.99954
DENSITY LOCALIZATION		MAGNASCO-PERICO LOCALIZATION	
	iLi	b $\sigma$ LiH	
1 $\sigma$	0.99477	0.10213	1 $\sigma$ 0.99010
2 $\sigma$	-0.10213	0.99477	2 $\sigma$ -0.14035
			0.99010

<sup>1</sup> The detailed results (basis set, expansion coefficients for the CMO's and LMO's and transformation matrices) can be obtained upon request from the author.

## LiF (Table 4)

For the LiF molecule one would anticipate a structure with a single bond and three lone pairs of electrons on the F atom. But Edmiston and Ruedenberg obtained besides the two inner shells a  $\sigma$ -type lone pair orbital on the F atom and three trigonally equivalent banana bonds strongly polarized towards the F atom [4]. Our calculations gave the following results: With the energy and the density localization method we obtained a single bond, but the methods of Boys and of Magnasco and Perico tended towards three strongly polarized banana bonds and a single lone pair which has a large  $2p\sigma$ -contribution. Since the method of Magnasco and Perico requires a concept of the LMO's for the calculation, it might thus be expected to yield any answer. But to the credit of this method it was found that only the three bond picture represents a solution. Obtaining each of the two possibilities twice is puzzling. But it should be recalled that, although the concept of the LMO's is a very convenient and useful one, it is basically arbitrary.

Table 4

## TRANSFORMATION MATRICES FOR LiF

## ENERGY LOCALIZATION

	iF	iLi	b $\sigma$ LiF	$\lambda t1F$	$\lambda t2F$	$\lambda t3F$
1 $\sigma$	0.98994	-0.00216	0.06848	0.07144	0.07160	0.07135
2 $\sigma$	-0.00560	0.99605	0.08756	0.00832	0.00669	0.00888
3 $\sigma$	-0.14082	-0.06058	0.55089	0.47394	0.47289	0.47411
4 $\sigma$	-0.01243	0.06493	-0.82685	0.31622	0.34279	0.30734
1 $\pi$	0.00001	-0.00013	0.02130	-0.00327	0.69702	-0.71673
	-0.00001	0.00006	-0.00632	0.81866	-0.40971	-0.40237

## DENSITY LOCALIZATION

	iF	iLi	b $\sigma$ LiF	$\lambda t1F$	$\lambda t2F$	$\lambda t3F$
1 $\sigma$	0.98040	-0.00521	0.09524	0.09989	0.09944	0.09924
2 $\sigma$	-0.00648	0.99152	0.12961	-0.00658	-0.00189	0.00019
3 $\sigma$	-0.19618	-0.06827	0.54243	0.46902	0.47019	0.47071
4 $\sigma$	-0.01685	0.11045	-0.82370	0.35427	0.31210	0.29345
1 $\pi$	0.00000	-0.00007	0.03215	0.78070	-0.57643	-0.23916
	-0.00000	0.00004	-0.01948	-0.18708	-0.58254	0.79074

## BOYS LOCALIZATION

	iF	iLi	bt1LiF	bt2LiF	bt3LiF	$\lambda\sigma F$
1 $\sigma$	0.99642	-0.00078	0.04160	0.04162	0.04162	0.04410
2 $\sigma$	-0.00407	0.99667	0.04591	0.04556	0.04544	-0.01957
3 $\sigma$	-0.08421	-0.06110	0.50869	0.50833	0.50820	0.46233
4 $\sigma$	-0.00575	0.05397	-0.27138	-0.26523	-0.26299	0.88538
1 $\pi$	-0.00001	-0.00001	-0.66038	0.74638	-0.08253	-0.00334
	-0.00001	-0.00001	-0.47713	-0.33221	0.81361	-0.00409

## MAGNASCO-PERICO LOCALIZATION

	iF	iLi	bt1LiF	bt2LiF	bt3LiF	$\lambda\sigma F$
1 $\sigma$	0.97437	-0.00528	0.08605	0.08605	0.08605	0.16844
2 $\sigma$	-0.00649	0.99310	0.06516	0.06516	0.06516	-0.03118
3 $\sigma$	-0.21922	-0.07371	0.45726	0.45726	0.45726	0.56501
4 $\sigma$	-0.05013	0.09106	-0.33555	-0.33555	-0.33555	0.80710
1 $\pi$	0.0	0.0	0.81650	-0.40825	-0.40825	0.0
	0.0	0.0	0.0	0.70711	-0.70711	0.0

For the particular case of LiF we can suggest a model to rationalize the results. Instead of regarding the LiF molecule as being covalently bonded we can regard it as an ionic structure with a partial covalent character. Essentially we would have  $\text{Li}^+ \text{F}^-$ . For the  $\text{F}^-$  ion we would obtain four tetrahedrally equivalent lone pair orbitals (see the results for the Ne atom in I). Because of the presence of the  $\text{Li}^+$  ion this tetrahedron will be distorted. Recalling the van't Hoff model for carbon compounds one could form a single bond by letting a corner of the tetrahedron point towards the  $\text{Li}^+$  ion, and a double or a triple bond by letting two or three lobes point in this direction. One could thus expect all three possibilities as the results of a localization. We have obtained two of them. Since we are dealing with different localization methods this is quite reasonable. With a different wavefunction it is feasible that the double bond picture could emerge, because a strong dependence of the results on the wavefunction is very probable. It could be

Table 5

## TRANSFORMATION MATRICES FOR BF

## ENERGY LOCALIZATION

	iF	iB	b $\sigma$ BF	$\lambda$ t1F	$\lambda$ t2F	$\lambda$ t3F	$\lambda\sigma$ B
1 $\sigma$	0.98970	-0.00081	0.06388	0.07395	0.07389	0.07380	-0.00692
2 $\sigma$	-0.00111	0.99293	0.05162	-0.00303	-0.00297	-0.00286	0.10680
3 $\sigma$	-0.13744	-0.03800	0.65201	0.42794	0.42787	0.42792	0.07226
4 $\sigma$	0.03868	-0.05896	0.73306	-0.38094	-0.37976	-0.37657	0.16282
1 $\pi$	-0.00001	0.00001	-0.00110	0.26498	-0.80069	0.53728	0.00003
5 $\sigma$	0.00001	-0.00001	0.00218	0.77135	-0.15834	-0.61639	-0.00002
5 $\sigma$	0.01084	-0.09579	-0.17537	0.03265	0.03247	0.03188	0.97817

## DENSITY LOCALIZATION

	iF	iB	b $\sigma$ BF	$\lambda$ t1F	$\lambda$ t2F	$\lambda$ t3F	$\lambda\sigma$ B
1 $\sigma$	0.97995	-0.00198	0.09173	0.10238	0.10203	0.10176	-0.00480
2 $\sigma$	-0.00091	0.98505	0.06654	-0.00865	-0.00813	-0.00773	0.15825
3 $\sigma$	-0.19120	-0.05242	0.64663	0.41934	0.41980	0.42011	0.11825
4 $\sigma$	0.05287	-0.08798	0.71860	-0.39026	-0.38147	-0.37476	0.18657
1 $\pi$	-0.00000	0.00000	-0.00414	-0.03374	-0.68666	0.72618	0.00007
5 $\sigma$	-0.00000	0.00001	-0.00779	-0.81208	0.44236	0.38051	0.00013
5 $\sigma$	0.01828	-0.13849	-0.22925	0.02617	0.02420	0.02271	0.96236

## BOYS LOCALIZATION

	iF	iB	b $\sigma$ BF	$\lambda$ t1F	$\lambda$ t2F	$\lambda$ t3F	$\lambda\sigma$ B
1 $\sigma$	0.99604	-0.00045	0.03256	0.04772	0.04772	0.04772	-0.00268
2 $\sigma$	-0.00084	0.99804	0.03564	0.00183	0.00183	0.00184	0.05139
3 $\sigma$	-0.08416	-0.02677	0.63980	0.44049	0.44049	0.44049	0.02760
4 $\sigma$	0.02854	-0.03274	0.75485	-0.36755	-0.36759	-0.36733	0.15218
1 $\pi$	-0.00000	0.0	-0.00005	-0.81646	0.41099	0.40556	-0.00000
5 $\sigma$	0.00000	0.00000	0.00014	0.00307	0.70547	-0.70874	0.00000
5 $\sigma$	0.00071	-0.04618	-0.13610	0.04440	0.04441	0.04437	0.98663

## MAGNUSCO-PERICO LOCALIZATION

	iF	iB	b $\sigma$ BF	$\lambda$ t1F	$\lambda$ t2F	$\lambda$ t3F	$\lambda\sigma$ B
1 $\sigma$	0.96748	-0.00303	0.07739	0.13901	0.13901	0.13901	-0.00110
2 $\sigma$	-0.00171	0.97468	0.08490	-0.00418	-0.00418	-0.00418	0.20670
3 $\sigma$	-0.23774	-0.05960	0.59356	0.44112	0.44112	0.44112	0.06204
4 $\sigma$	0.08573	-0.08903	0.78787	-0.34555	-0.34555	-0.34555	0.07596
1 $\pi$	0.0	0.0	0.0	0.81650	-0.40825	-0.40825	0.0
5 $\sigma$	0.0	0.0	0.0	0.0	-0.70711	0.70711	0.0
5 $\sigma$	0.00991	-0.19622	-0.11724	-0.00011	-0.00011	-0.00011	0.97348

argued that we have the case of multiple extrema, some localization methods find one minimum, others a second one. But although this cannot be ruled out, it was made improbable by taking different starting points and examining another wavefunction with a smaller basis set. Our model is supported when we consider the charge centroids of the LMO's. For the ELMO's (DLMO's) the charge centroids of the lone pair orbitals are at a distance of about 0.52 a.u. (0.52 a.u.) from the F atom and of the bond orbital at a distance of about 0.57 a.u. (0.58 a.u.). For the BLMO's (MPLMO's) the charge centroid of the lone pair orbital is at a distance of about 0.52 a.u. (0.57 a.u.) from the F atom and for the three bond orbitals at a distance of about 0.54 a.u. (0.51 a.u.). This is consistent in all cases with the model of a distorted tetrahedron of LMO's surrounding the F atom. The transformation matrices are given in Table 4.

#### BF (Table 5)

Edmiston and Ruedenberg obtained for the BF molecule (as for the LiF molecule) three polarized bond orbitals and a  $\sigma$ -type lone pair orbital on the B and on the F atom (besides the inner shells). They stated that in addition the F lone pair orbital seemed to have gained some bonding character. In the case of the wavefunction we are examining all four localization methods gave the same answer which was a single bond orbital connecting the B and F atoms and polarized towards the latter, a single lone pair orbital on the B atom and three lone pair orbitals on the F atom (Table 5). In this case the ionic model does not seem to be so appropriate.

#### BN (Table 6)

To the knowledge of the author no LMO's have so far been obtained for the BN molecule. (We consider the  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4, {}^1\Sigma^+$  state.) In this case again the different localization methods yield different results. An anticipated structure would involve, besides the obligatory inner shells on the B and N atoms, a triple bond polarized towards the N atom and a lone pair of electrons on the N atom. This picture is found with the energy, the Boys and the Magnasco-Perico method, but the N-lone pair is found to have a fairly strong bonding character (Table 6). This is seen from the relatively large coefficients of the B atom s-type functions contributing to this lone pair orbital. The charge centroid of this orbital is only at a distance of about 0.14 a.u. from the N atom. A similar result was found by Edmiston and Ruedenberg for the F-lone pair orbital in BF [4]. The three trigonally equivalent BN bond orbitals are slightly polarized towards the N atom. The agreement between the results of the method of Boys and of Magnasco and Perico is quite good, between the ELMO's and the BLMO's only fair, although these generally agree well. The density localization method gives on a first superficial examination the picture of a double bond and two lone pairs of electrons on the N atom. But a closer investigation reveals that the lone pair orbitals are strange in so far as they are turned inside the bond region towards the B atom. They seem to be hybrids between bond and lone pair orbitals and one could call them lone pair orbitals which have become bonding in character. Peters [18] obtained with his localization method hybrids which pointed in the



Table 6

TRANSFORMATION MATRICES FOR BN						
ENERGY LOCALIZATION						
	1N	1B	$\lambda\sigma N$	bt1BN	bt2BN	bt3BN
1 $\sigma$	0.99145	-0.00192	0.09844	0.04945	0.04943	0.04943
2 $\sigma$	-0.00167	0.99440	-0.04632	0.05488	0.05486	0.05477
3 $\sigma$	-0.11637	-0.07058	0.37190	0.53041	0.53018	0.52984
4 $\sigma$	0.05900	-0.07864	-0.92187	0.21681	0.21652	0.21586
1 $\pi$	0.00001	-0.00001	-0.00025	-0.79182	0.56802	0.22447
	-0.00000	-0.00000	0.00041	0.19806	0.58646	-0.78539
DENSITY LOCALIZATION						
	1N	1B	bd1BN	bd2BN	$\lambda d1N$	$\lambda d2N$
1 $\sigma$	0.98207	-0.00390	0.07990	0.07991	0.10666	0.10665
2 $\sigma$	-0.00201	0.98703	0.10226	0.10223	-0.04931	-0.04934
3 $\sigma$	-0.16817	-0.09866	0.62227	0.62224	0.30631	0.30622
4 $\sigma$	0.08515	-0.12661	0.30988	0.30968	-0.62633	-0.62650
1 $\pi$	0.0	0.0	0.45405	-0.45425	0.54208	-0.54189
	0.0	-0.00000	0.54199	-0.54198	-0.45412	0.45418
BOYS LOCALIZATION						
	1N	1B	$\lambda\sigma N$	bt1BN	bt2BN	bt3BN
1 $\sigma$	0.99690	-0.00094	0.06660	0.02413	0.02413	0.02413
2 $\sigma$	-0.00125	0.99860	-0.00035	0.03052	0.03052	0.03052
3 $\sigma$	-0.07109	-0.04435	0.53663	0.48477	0.48477	0.48477
4 $\sigma$	0.03358	-0.02878	-0.84119	0.31115	0.31115	0.31115
1 $\pi$	0.0	0.0	-0.00000	0.57849	-0.78825	0.20976
	0.0	0.0	-0.00000	0.57620	0.21289	-0.78909
MAGNASCO-PERICO LOCALIZATION						
	1N	1B	$\lambda\sigma N$	bt1BN	bt2BN	bt3BN
1 $\sigma$	0.96506	-0.01481	0.25260	0.03928	0.03928	0.03928
2 $\sigma$	-0.00629	0.99594	0.00105	0.16944	0.16944	0.16944
3 $\sigma$	-0.23728	-0.19001	0.73076	0.35288	0.35288	0.35288
4 $\sigma$	0.11096	-0.22327	-0.63418	0.42256	0.42256	0.42256
1 $\pi$	0.0	0.0	0.0	0.81650	-0.40825	-0.40825
	0.0	0.0	0.0	0.0	0.70711	-0.70711

wrong direction from what they should. He called them negative hybrids. We have examined whether such negative hybrids can arise as well with the intrinsic density localization method. But this was not found. The hybrids on the N atom (which are used to construct the lone pair orbitals) do not point into the bonding region but away from it. It is the contributions from the B atom which cause the orbitals to have their charge centroids within the bonding region. They have consequently gained substantial bonding character. We thus obtain for the BN molecule either three bond orbitals and a partially bonding N-lone pair orbital or two bond orbitals and two partially bonding lone pair orbitals on the N atom. Since the DLMO's can also be regarded as giving the picture of a quadruple bond one could argue that this result does not make too much sense, because such a bond is unknown in chemistry. Also the other result of a  $\sigma$ -type lone pair orbital which has gained some bonding character does not make too much sense either in view of the classical chemical concepts. But it should be noted that both concepts, the classical chemical ones as well as the concept of the LMO's are basically arbitrary and derive their justification from their usefulness.

## CO (Table 7)

The energy and the Boys localization method give an inner shell and a lone pair orbital on each atom and a set of trigonal bond orbitals polarized towards the O atom. Both lone pair orbitals have gained a partial bonding character, but a much smaller one than in the case of the BN molecule. With the density localization method we obtain a lone pair orbital on the C atom, a  $\sigma$ -type bond orbital slightly polarized towards the O atom and three lone pair orbitals on the O atom which are partially bonding in character so that their charge centroids fall

Table 7

## TRANSFORMATION MATRICES FOR CO

## ENERGY LOCALIZATION

	1O	1C	$\lambda\sigma O$	bt1CO	bt2CO	bt3CO	$\lambda\sigma C$
1 $\sigma$	0.99057	-0.00110	0.09317	-0.05765	-0.05763	-0.05750	-0.01154
2 $\sigma$	-0.00158	0.99203	-0.02532	-0.03652	-0.03642	-0.03552	0.10639
3 $\sigma$	-0.11875	-0.06614	0.26123	-0.55041	-0.54937	-0.54258	0.11890
4 $\sigma$	-0.06816	0.07132	0.91692	0.12910	0.12769	0.11718	-0.32065
	-0.00001	0.00002	-0.00531	0.80989	-0.34661	-0.47320	-0.00005
1 $\pi$	-0.00001	-0.00005	0.00607	0.07683	-0.73712	0.67135	0.00008
5 $\sigma$	0.00414	-0.08015	0.28569	0.11793	0.11730	0.11260	0.93359

## BOYS LOCALIZATION

	1O	1C	$\lambda\sigma O$	bt1CO	bt2CO	bt3CO	$\lambda\sigma C$
1 $\sigma$	0.99688	-0.00057	0.05256	0.03387	0.03387	0.03387	-0.00510
2 $\sigma$	-0.00124	0.99732	-0.01141	0.02643	0.02643	0.02643	0.05599
3 $\sigma$	-0.07110	-0.04406	0.29455	0.54826	0.54826	0.54826	0.06695
4 $\sigma$	-0.03427	0.03945	0.91478	-0.15195	-0.15195	-0.15195	-0.30195
	0.00000	0.0	0.00000	0.81593	-0.43423	-0.38170	0.00000
1 $\pi$	-0.00000	0.0	0.0	0.03033	0.69146	-0.72178	-0.00000
5 $\sigma$	-0.00045	-0.04317	0.27115	-0.08838	-0.08837	-0.08838	0.94931

## MAGNASCO-PERICO LOCALIZATION A

	1O	1C	$\lambda\sigma O$	bt1CO	bt2CO	bt3CO	$\lambda\sigma C$
1 $\sigma$	0.98035	-0.00361	0.17653	0.05075	0.05075	0.05075	-0.00395
2 $\sigma$	-0.00318	0.98219	-0.01055	0.06005	0.06005	0.06005	0.15609
3 $\sigma$	-0.17352	-0.10166	0.58042	0.44604	0.44604	0.44604	0.16063
4 $\sigma$	-0.09363	0.11019	0.78196	-0.30859	-0.30859	-0.30859	-0.28628
	0.0	0.0	0.0	0.40825	0.40825	-0.81650	0.0
1 $\pi$	0.0	0.0	0.0	0.70711	-0.70711	0.0	0.0
5 $\sigma$	0.00584	-0.11320	0.14273	-0.18158	-0.18158	-0.18158	0.93159

## DENSITY LOCALIZATION

	1O	1C	b $\sigma$ CO	$\lambda t1O$	$\lambda t2O$	$\lambda t3O$	$\lambda\sigma C$
1 $\sigma$	0.98104	-0.00267	0.09119	0.09897	0.09849	0.09822	-0.00992
2 $\sigma$	-0.00171	0.98303	0.09337	-0.00934	-0.00892	-0.00866	0.15710
3 $\sigma$	-0.16765	-0.09559	0.79382	0.31619	0.31658	0.31692	0.17881
4 $\sigma$	-0.09671	0.10956	-0.48817	0.46680	0.46096	0.45748	-0.31729
	-0.00000	0.00000	-0.00447	-0.79681	0.26185	0.54453	0.00014
1 $\pi$	-0.00000	0.00000	-0.00085	0.16377	-0.77389	0.61178	0.00002
5 $\sigma$	0.01013	-0.11178	-0.33837	0.10254	0.10023	0.09884	0.91792

## MAGNASCO-PERICO LOCALIZATION B

	1O	1C	b $\sigma$ CO	$\lambda t1O$	$\lambda t2O$	$\lambda t3O$	$\lambda\sigma C$
1 $\sigma$	0.98035	-0.00361	0.08791	0.10192	0.10192	0.10192	-0.00395
2 $\sigma$	-0.00318	0.98219	0.10400	-0.00609	-0.00609	-0.00609	0.15609
3 $\sigma$	-0.17352	-0.10166	0.77257	0.33511	0.33511	0.33511	0.16063
4 $\sigma$	-0.09363	0.11019	-0.53449	0.45146	0.45146	0.45146	-0.28628
	0.0	0.0	0.0	0.81650	-0.40825	-0.40825	0.0
1 $\pi$	0.0	0.0	0.0	0.0	-0.70711	0.70711	0.0
5 $\sigma$	0.00584	-0.11320	-0.31451	0.08241	0.08241	0.08241	0.93159

into the bonding region (by about 0.15 a.u.) instead of outside. Starting with the ELMO's instead of the CMO's as input to the density localization calculation, results identical with the DLMO's as described above were obtained eliminating the possibility of a second minimum. Using the IBMOL Version 4 program (which uses the Cartesian Gaussian functions as basis functions) a calculation was performed for the CO molecule to check the results for the DLMO's. Complete agreement was found between the results of the two wavefunctions. The Magnasco-Perico method can give both results, three bond orbitals (A in Table 7) or three partially bonding lone pair and one bond orbital (B in Table 7) depending on which  $\sigma$ -orbital is mixed with the  $\pi$ -orbitals.

### $C_2H_2$ (Table 8)

The structure of acetylene is similar to the structure of nitrogen which was discussed in II. We obtain two inner shells, two equivalent CH bond orbitals and three equivalent CC' bond orbitals (Table 8). These bond orbitals have a

Table 8

TRANSFORMATION MATRICES FOR  $C_2H_2$ 

## ENERGY LOCALIZATION

	1C	1C'	b $\sigma$ CH	b $\sigma$ C'H'	bt1CC'	bt2CC'	bt3CC'
1 $\sigma_{g_g}$	0.70059	0.70059	0.04189	0.04189	0.07034	0.07034	0.07024
1 $\sigma_{u_u}$	0.70465	-0.70465	0.05893	-0.05894	-0.00000	-0.00000	0.00000
2 $\sigma_{g_g}$	-0.09556	-0.09557	0.26556	0.26557	0.52961	0.52959	0.52890
2 $\sigma_{u_u}$	-0.05893	0.05894	0.70464	-0.70465	-0.00001	0.00002	0.00000
3 $\sigma_{g_g}$	-0.00607	-0.00607	0.65401	0.65400	-0.21961	-0.21959	-0.21916
3 $\sigma_{u_u}$	-0.00000	0.00000	0.00006	0.00004	0.81572	-0.38213	-0.43425
1 $\pi_u$	-0.00000	0.00001	-0.00005	-0.00007	0.03042	-0.72135	0.69190

## DENSITY LOCALIZATION

	1C	1C'	b $\sigma$ CH	b $\sigma$ C'H'	bt1CC'	bt2CC'	bt3CC'
1 $\sigma_{g_g}$	0.69332	0.69332	0.06057	0.06057	0.10248	0.10202	0.10186
1 $\sigma_{u_u}$	0.70135	-0.70135	0.09005	-0.09005	0.0	0.0	0.00000
2 $\sigma_{g_g}$	-0.13876	-0.13876	0.26722	0.26722	0.52425	0.52186	0.52106
2 $\sigma_{u_u}$	-0.09005	0.09005	0.70135	-0.70135	-0.00000	-0.00000	0.00000
3 $\sigma_{g_g}$	-0.00754	-0.00754	0.65186	0.65186	-0.22486	-0.22328	-0.22276
3 $\sigma_{u_u}$	0.00000	0.00000	0.00035	0.00035	0.79008	-0.22455	-0.57039
1 $\pi_u$	0.0	0.0	-0.00000	-0.00000	-0.19967	0.78548	-0.58580

## BOYS LOCALIZATION

	1C	1C'	b $\sigma$ CH	b $\sigma$ C'H'	bt1CC'	bt2CC'	bt3CC'
1 $\sigma_{g_g}$	0.70500	0.70501	0.01994	0.01994	0.04139	0.04139	0.04139
1 $\sigma_{u_u}$	0.70663	-0.70663	0.02601	-0.02601	0.0	-0.00000	0.00000
2 $\sigma_{g_g}$	-0.05448	-0.05448	0.25290	0.25290	0.53732	0.53732	0.53732
2 $\sigma_{u_u}$	-0.02601	0.02601	0.70663	-0.70663	0.0	0.0	0.0
3 $\sigma_{g_g}$	-0.00043	-0.00043	0.66003	0.66003	-0.20713	-0.20713	-0.20713
3 $\sigma_{u_u}$	0.00000	0.00000	0.0	0.0	-0.37846	0.81579	-0.43733
1 $\pi_u$	0.0	0.00000	0.0	0.0	-0.72349	0.03399	0.68950

## MAGNASCO-PERICO LOCALIZATION

	1C	1C'	b $\sigma$ CH	b $\sigma$ C'H'	bt1CC'	bt2CC'	bt3CC'
1 $\sigma_{g_g}$	0.69185	0.69185	0.06723	0.06723	0.10592	0.10592	0.10592
1 $\sigma_{u_u}$	0.70070	-0.70070	0.09500	-0.09500	0.0	0.0	0.0
2 $\sigma_{g_g}$	-0.14551	-0.14551	0.26015	0.26015	0.52355	0.52355	0.52355
2 $\sigma_{u_u}$	-0.09500	0.09500	0.70070	-0.70070	0.0	0.0	0.0
3 $\sigma_{g_g}$	-0.01324	-0.01324	0.65407	0.65407	-0.21912	-0.21912	-0.21912
3 $\sigma_{u_u}$	0.0	0.0	0.0	0.0	-0.77125	0.15350	0.61775
1 $\pi_u$	0.0	0.0	0.0	0.0	-0.26803	0.80194	-0.53391

Table 10

TRANSFORMATION MATRICES FOR NH<sub>3</sub>

ENERGY LOCALIZATION			
	iN	bσNH	ℓσN
1a <sub>1</sub>	0.99262	0.05477	0.05477
2a <sub>1</sub>	-0.11410	0.54359	0.54367
1e	0.00000	0.81655	-0.40820
3a <sub>1</sub>	-0.00000	-0.00002	0.70710
	-0.04110	-0.18642	-0.18653

## DENSITY LOCALIZATION

	iN	bσNH	ℓσN
1a <sub>1</sub>	0.98452	0.08016	0.08022
2a <sub>1</sub>	-0.16611	0.53897	0.53940
1e	0.00001	0.81676	-0.40799
3a <sub>1</sub>	-0.00000	0.0	0.70711
	-0.05588	-0.18970	-0.19014

## BOYS LOCALIZATION

	iN	bσNH	ℓσN
1a <sub>1</sub>	0.99755	0.02812	0.02812
2a <sub>1</sub>	-0.06199	0.54756	0.54751
1e	0.00000	0.81647	-0.40827
3a <sub>1</sub>	0.0	0.0	0.70711
	-0.03256	-0.18101	-0.18099

## MAGNASC0-PERICO LOCALIZATION

	iN	bσNH	ℓσN
1a <sub>1</sub>	0.98151	0.08932	0.08932
2a <sub>1</sub>	-0.17251	0.56015	0.56006
1e	0.00002	-0.81646	-0.40829
3a <sub>1</sub>	0.0	0.0	0.70711
	-0.08293	-0.10793	-0.10797

Table 9

TRANSFORMATION MATRICES FOR CH<sub>4</sub>

ENERGY LOCALIZATION			
	iC	bσCH	ℓσN
1a <sub>1</sub>	0.99420	0.05380	0.05380
2a <sub>1</sub>	-0.10759	0.49710	0.49710
1t <sub>2</sub>	0.00000	0.10111	-0.47425
	-0.00000	-0.13504	0.75607
	-0.00000	0.84943	-0.33963

## DENSITY LOCALIZATION

	iC	bσCH	ℓσN
1a <sub>1</sub>	0.98727	0.07953	0.07953
2a <sub>1</sub>	-0.15907	0.49363	0.49363
1t <sub>2</sub>	0.0	0.10112	-0.47426
	0.0	-0.13503	0.75608
	0.0	0.84944	-0.33961

## BOYS LOCALIZATION

	iC	bσCH	ℓσN
1a <sub>1</sub>	0.99836	0.02862	0.02862
2a <sub>1</sub>	-0.05724	0.49918	0.49918
1t <sub>2</sub>	0.00000	0.10112	-0.47426
	-0.00000	-0.13503	0.75608
	-0.00000	0.84944	-0.33961

## MAGNASC0-PERICO LOCALIZATION

	iC	bσCH	ℓσN
1a <sub>1</sub>	0.97589	0.10913	0.10913
2a <sub>1</sub>	-0.21826	0.48795	0.48795
1t <sub>2</sub>	0.0	0.10112	-0.47426
	0.0	-0.13503	0.75608
	0.0	0.84944	-0.33961

Table 11

## TRANSFORMATION MATRICES FOR H2O

## ENERGY LOCALIZATION

iO	bcOH	bcOH'	ld10	ld20
1a1	0.99106	0.05675	0.07539	0.07538
2a1	-0.12370	0.60253	0.35962	0.35957
1b2	-0.00001	0.70710	-0.00000	0.0
3a1	-0.05003	-0.36571	0.60410	0.60422
1b1	0.00001	0.00005	-0.70715	0.70707

## DENSITY LOCALIZATION

iO	bcOH	bcOH'	ld10	ld20
1a1	0.98209	0.08155	0.10534	0.10535
2a1	-0.17596	0.59683	0.35821	0.35821
1b2	0.0	0.70711	-0.00000	0.00000
3a1	-0.06732	-0.37034	0.60048	0.60050
1b1	0.0	0.00000	-0.70711	0.70710

## BOYS LOCALIZATION

iO	bcOH	bcOH'	ld10	ld20
1a1	0.99671	0.03034	0.04860	0.04860
2a1	-0.07175	0.60915	0.35548	0.35548
1b2	0.00000	0.70711	-0.00000	0.00000
3a1	-0.03764	-0.35780	0.60932	0.60932
1b1	0.00000	0.00000	-0.70711	0.70711

## MAGNASCO-PERICO LOCALIZATION

iO	bcOH	bcOH'	ld10	ld20
1a1	0.97584	0.09367	0.12285	0.12285
2a1	-0.19152	0.63734	0.27469	0.27469
1b2	0.00000	0.70711	-0.00000	-0.00000
3a1	-0.10513	-0.29158	0.63989	0.63989
1b1	0.0	0.0	-0.70711	0.70711

Table 12

## TRANSFORMATION MATRICES FOR HF

## ENERGY LOCALIZATION

iF	bcHF	lt1F	lt2F	lt3F
1σ	0.98973	0.05279	0.07676	0.07665
2σ	-0.13733	0.60909	0.45129	0.45079
3σ	0.03967	0.79135	-0.35294	-0.35196
1π	-0.00001	-0.00046	-0.79743	0.24945
	0.00001	0.00003	0.17316	-0.77765
				0.60438

## DENSITY LOCALIZATION

iF	bcHF	lt1F	lt2F	lt3F
1σ	0.98010	0.07618	0.10603	0.10589
2σ	-0.19152	0.60546	0.44649	0.44533
3σ	0.05212	0.79222	-0.35330	-0.35181
1π	-0.00000	-0.00098	-0.30243	0.80723
	-0.00000	-0.00235	-0.75705	0.11968
				0.64230

## BOYS LOCALIZATION

iF	bcHF	lt1F	lt2F	lt3F
1σ	0.99600	0.02898	0.04881	0.04881
2σ	-0.08411	0.62365	0.44870	0.44870
3σ	0.03020	0.78116	-0.36003	-0.36003
1π	-0.00000	0.00000	0.75396	-0.10557
	0.00000	0.0	-0.80964	0.64839
				-0.49625

## MAGNASCO-PERICO LOCALIZATION

iF	bcHF	lt1F	lt2F	lt3F
1σ	0.96579	0.09579	0.13913	0.13913
2σ	-0.25126	0.57554	0.44930	0.44930
3σ	0.06415	0.81214	-0.33482	-0.33482
1π	0.0	0.0	0.61957	-0.77033
	0.0	0.0	-0.53178	-0.27068
				0.80246

Table 13. Angles between bond and lone pair orbitals and hybrids resulting from different localization methods in H<sub>2</sub>O and NH<sub>3</sub><sup>a</sup>

Angle formed by	ELMO	DLMO	BLMO	MPLMO
OH bond orbitals	103°	102°	103.5°	107°
O-hybrids for bond orbitals	96°	93°	96.5°	104°
O-lone pair orbitals	114°	116°	113.5°	110°
O-hybrids for lone pair orbitals	115.5°	117.5°	116°	110.5°
NH bond orbitals	106°	105.5°	106°	109°
N-hybrids for bond orbitals	101.5°	100°	102°	109°

<sup>a</sup> The experimental values are  $\angle$  HOH = 104.45°,  $\angle$  HNH = 107°.

smaller *2p*-character than the corresponding orbitals in N<sub>2</sub>, a fact anticipated by Hall and Lennard-Jones [19]. The CH bond orbital is slightly polarized towards the H atom as measured by the charge centroids.

#### CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HF (Tables 9, 10, 11, 12, 13)

Finally we consider the molecules CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and HF. We obtain upon localization for each molecule an inner shell orbital, 4, 3, 2, and 1 equivalent XH bond orbitals and 0, 1, 2, and 3 equivalent lone pair orbitals respectively. The CH bond orbital is polarized towards the H atom as is the NH and the OH bond orbital as measured by the charge centroids, only the FH bond orbital is slightly polarized towards the heavy atom. In LiF the bond orbital (for ELMO's and DLMO's) was much more polarized towards the F atom in agreement with the very polar structure of LiF. The results for the different localization methods are numerically in good agreement with each other for the CH<sub>4</sub> and FH molecules, but for NH<sub>3</sub> and H<sub>2</sub>O the MPLMO's differ appreciably from the other results. (For the transformation matrices see Tables 9 (CH<sub>4</sub>), 10 (NH<sub>3</sub>), 11 (H<sub>2</sub>O), and 12 (HF).)

In Table 13 we give for the molecules H<sub>2</sub>O and NH<sub>3</sub> the angles between the bond orbitals, between the lone pair orbitals, and the angles between the hybrids leading to these orbitals. The experimental angle between the two OH bonds in H<sub>2</sub>O is 104.45°, between two NH bonds in NH<sub>3</sub> approximately 107°. We conclude from the table that the angles between the bond orbitals all agree reasonably well with the experimental values. The angles formed by the hybrids resulting from the Magnasco-Perico method agree best with the angles formed by the internuclear directions. In addition the Magnasco-Perico bond orbitals show the smallest degree of bending whereas the DLMO's show the greatest one.

#### 4. Analysis of the Hybrids

A number of theories have been developed to calculate approximate wave-functions by starting with the construction of optimal hybrids and combining them to one and two center LMO's [20]. These theories require a concept of the orbital

structure and of the structure of these hybrids. The problem of constructing these hybrids becomes certainly much more difficult when extended basis sets are used for the calculations. This is one reason for examining the hybrids which result without a preconception from the application of the localization methods to SCF wavefunctions. We obtain information on the differences in the structure of the hybrids resulting from the different methods and thus obtain information on the behaviour of the methods in applications. Also we are looking for trends in the structure of hybrids and the similarity of hybrids contributed to the same type of LMO for a fixed atom in different molecules. (Because we consider only

Table 14.  $s$ ,  $2p\sigma$ , and  $2p\pi$ -type populations of normalized hybrids on different atoms in localized lone pair orbitals

Atom	Type	ELMO	DLMO	BLMO	MPLMO
Be in Be <sub>2</sub>	$s$	0.9996	0.9996	0.9996	0.9997
	$2p\sigma$	0.0004	0.0004	0.0004	0.0003
B in B <sub>2</sub>	$s$	0.8269	0.8322	0.8219	0.8609
	$2p\sigma$	0.1731	0.1678	0.1781	0.1391
B in BF	$s$	0.8990	0.9055	0.8944	0.8927
	$2p\sigma$	0.1010	0.0945	0.1056	0.1073
C in CO	$s$	0.8465	0.8592	0.8312	0.8498 <sup>a,b</sup>
	$2p\sigma$	0.1535	0.1408	0.1688	0.1502 <sup>a,b</sup>
N in N <sub>2</sub>	$s$	0.7666	0.7863	0.7543	0.8353
	$2p\sigma$	0.2334	0.2137	0.2457	0.1647
N in BN	$s$	0.7577	0.5177	0.8380	0.9377
	$2p\sigma$	0.2423	0.1339	0.1620	0.0623
	$2p\pi$	0	0.3484	0	0
N in NH <sub>3</sub>	$s$	0.3084	0.3128	0.3016	0.2154
	$2p$	0.6916	0.6872	0.6984	0.7846
O in CO	$s$	0.5835	0.3504	0.6076	0.8317 <sup>a</sup>
					0.3633 <sup>b</sup>
	$2p\sigma$	0.4164	0.0846	0.3924	0.1683 <sup>a</sup>
	$2p\pi$	0.0001	0.5650	0	0.0735 <sup>b</sup>
O in H <sub>2</sub> O	$s$	0.3186	0.3213	0.3139	0.2739
	$2p\sigma$	0.1951	0.1925	0.1995	0.2370
	$2p\pi$	0.4863	0.4862	0.4866	0.4891
	$s$	0.3282	0.3303	0.3210	0.3264
F in F <sub>2</sub>	$2p\sigma$	0.0133	0.0103	0.0197	0.0145
	$2p\pi$	0.6585	0.6594	0.6593	0.6591
	$s$	0.2531	0.2537	0.2908	0.4263
F in LiF	$2p\sigma$	0.0797	0.0776	0.7092	0.5737
	$2p\pi$	0.6672	0.6687	0.0000	0
	$s$	0.2862	0.2855	0.2895	0.3085
F in BF	$2p\sigma$	0.0724	0.0726	0.0676	0.0522
	$2p\pi$	0.6414	0.6419	0.6429	0.6393
	$s$	0.2945	0.2953	0.2917	0.3004
F in HF	$2p\sigma$	0.0493	0.0494	0.0522	0.0436
	$2p\pi$	0.6563	0.6553	0.6561	0.6560

<sup>a</sup> MPLMO's corresponding to ELMO's.

<sup>b</sup> MPLMO's corresponding to DLMO's.

small molecules this is possible only in a few cases.) Because of limitation of space we do not give the expansion form of the hybrids. We present only the results for a particular aspect of the problem, we are going to analyze the  $s$ ,  $2p\sigma$ , and  $2p\pi$  character of the hybrids which are contributed by the atoms to the localized lone pair and bond orbitals. In Table 14 we give the  $s$ ,  $2p\sigma$ , and  $2p\pi$ -type populations in localized lone pair orbitals for normalized hybrids on different atoms. Table 15 contains the equivalent information for the bond orbitals. We have compiled the data of II and the present work. One should not attach too much importance to the numbers or to a disagreement among the methods because we refer to normalized hybrids which do not reflect the weight of these hybrids in the LMO.

Let us consider first the lone pair orbitals. There is one salient overall trend, which is very reasonable. If we regard the atoms from Be to F the  $2p$  contribution to the hybrids steadily increases with one marked exception – the hybrid leading to the lone pair orbital in  $\text{NH}_3$ . This has an extremely large  $2p$  character leading to the large extension of the lone pair orbital into the direction away from the rest of the molecule in congruence with its chemical behaviour. The Be hybrid in  $\text{Be}_2$  is practically a  $2s$  atomic orbital, so are the hybrids on the B atom. The  $s$ -character steadily decreases with increasing atomic number, but for atoms having only one lone pair orbital the  $s$ -character remains dominant with the noted exception of  $\text{NH}_3$ . The same trend can be observed for the hybrids on atoms with three lone pair orbitals. (See e.g.  $\text{XF}$ ,  $\text{X} = \text{H, Li, B, F}$ .) An increase of the  $2p$  character is necessary in going from one to several lone pair orbitals on the same atom, because these lone pair orbitals have to have a stronger directional

Table 15.  $s$ ,  $2p\sigma$ , and  $2p\pi$ -type populations of normalized hybrids on different atoms in localized bond orbitals

Atom	Type	ELMO	DLMO	BLMO	MPLMO
Li in $\text{Li}_2$	$s$	0.9973	0.9974	0.9973	0.9975
	$2p\sigma$	0.0027	0.0026	0.0027	0.0025
Li in LiH	$s$	0.9126	0.9116	0.9171	0.9144
	$2p\sigma$	0.0874	0.0884	0.0829	0.0856
Li in LiF	$s$	0.4837	0.2193	0.3693	0.1927
	$2p\sigma$	0.5162	0.7804	0.3134	0.4394
	$2p\pi$	0.0001	0.0003	0.3173	0.3679
B in $\text{B}_2$	$s$	0.3340	0.3121	0.3573	0.1958
	$2p\sigma$	0.6660	0.6879	0.6427	0.8042
B in BF	$s$	0.1403	0.1294	0.2155	0.2455
	$2p\sigma$	0.8597	0.8706	0.7845	0.7545
B in BN	$s$	0.2905	0.4704	0.3528	0.4367
	$2p\sigma$	0.0391	0.0537	0.0344	0.0221
	$2p\pi$	0.6704	0.4759	0.6128	0.5412
C in $\text{C}_2$	$s$	0.6982	0.6988 <sup>a</sup>	0.9925 <sup>d</sup>	—
			0.4037 <sup>b</sup>	0.0060 <sup>e</sup>	—
			0.6543 <sup>c</sup>	0.1409 <sup>f</sup>	—
			—	0.9120 <sup>g</sup>	—
			—	0.0075 <sup>d</sup>	—
	$2p\sigma$	0.0014	0.0014 <sup>a</sup>	0.0075 <sup>d</sup>	—
—	—	0.0431 <sup>b</sup>	0.0830 <sup>e</sup>	—	
—	—	0.0283 <sup>c</sup>	0.0155 <sup>f</sup>	—	
—	—	—	0.0041 <sup>g</sup>	—	



Table 15 (Continued)

Atom	Type	ELMO	DLMO	BLMO	MPLMO
C in C <sub>2</sub>	2p $\pi$	0.3004	0.2998 <sup>a</sup>	0.0 <sup>d</sup>	—
			0.5532 <sup>b</sup>	0.9110 <sup>e</sup>	
			0.3174 <sup>c</sup>	0.8436 <sup>f</sup>	
				0.0839 <sup>g</sup>	
C in CO	s	0.0782	0.1708	0.1286	0.0848 <sup>h</sup>
	2p $\sigma$	0.2250	0.8292	0.1903	0.2297 <sup>i</sup>
	2p $\pi$	0.6968	0.0000	0.6811	0.2843 <sup>h</sup>
C in C <sub>2</sub> H <sub>2</sub>	s	0.4348	0.4421	0.4212	0.7703 <sup>i</sup>
	2p $\sigma$	0.5652	0.5579	0.5788	0.6309 <sup>h</sup>
(CH bond)	s	0.1783	0.1763	0.1847	0.0 <sup>i</sup>
	2p $\sigma$	0.1118	0.1123	0.1066	0.4380
C in C <sub>2</sub> H <sub>2</sub>	s	0.1783	0.1763	0.1847	0.5620
	2p $\sigma$	0.1118	0.1123	0.1066	0.1789
(CC bond)	2p $\pi$	0.7099	0.7115	0.7087	0.1104
	s	0.3221	0.3235	0.3218	0.7107
C in CH <sub>4</sub>	2p	0.6779	0.6765	0.6782	0.3266
	s	0.1322	0.1115	0.1464	0.6734
N in N <sub>2</sub>	s	0.1322	0.1115	0.1464	0.0580
	2p $\sigma$	0.1497	0.1805	0.1349	0.2350
	2p $\pi$	0.7181	0.7080	0.7187	0.7070
N in BN	s	0.1668	0.2082	0.0789	0.0042
	2p $\sigma$	0.0995	0.1902	0.1541	0.2128
	2p $\pi$	0.7337	0.6016	0.7670	0.7830
N in NH <sub>3</sub>	s	0.2915	0.2898	0.2960	0.3610
	2p	0.7085	0.7102	0.7040	0.6390
O in CO	s	0.1941	0.2257	0.1746	0.0463 <sup>h</sup>
	2p $\sigma$	0.1021	0.7743	0.1066	0.1717 <sup>i</sup>
	2p $\pi$	0.7038	0.0000	0.7187	0.2234 <sup>h</sup>
O in H <sub>2</sub> O	s	0.2250	0.2210	0.2343	0.8283 <sup>i</sup>
	2p $\sigma$	0.7750	0.7790	0.7657	0.7303 <sup>h</sup>
F in F <sub>2</sub>	s	0.0380	0.0189	0.0937	0 <sup>i</sup>
	2p $\sigma$	0.9620	0.9811	0.9063	0.3187
F in LiF	s	0.2450	0.2441	0.2378	0.6813
	2p $\sigma$	0.7545	0.7544	0.0889	0.0498
	2p $\pi$	0.0005	0.0015	0.6734	0.9502
F in BF	s	0.2337	0.2451	0.2067	0.1923
	2p $\sigma$	0.7663	0.7549	0.7933	0.1292
F in HF	s	0.1570	0.1570	0.1732	0.6786
	2p $\sigma$	0.8430	0.8430	0.8268	0.1589

<sup>a</sup> DLMO A (see Ref. [2]).

<sup>b</sup> DLMO B (symmetric bonding orbital b3CC', b4CC', see Ref. [2]).

<sup>c</sup> DLMO B (unsymmetric bonding orbital b1CC', b2CC', see Ref. [2]).

<sup>d</sup> BLMO A (orbital b1CC', see Ref. [2]).

<sup>e</sup> BLMO A (orbital b2CC', b3CC', b4CC', see Ref. [2]).

<sup>f</sup> BLMO B (symmetric bonding orbital b3CC', b4CC', see Ref. [2]).

<sup>g</sup> BLMO B (unsymmetric bonding orbital b1CC', b2CC', see Ref. [2]).

<sup>h</sup> MPLMO's corresponding to ELMO's.

<sup>i</sup> MPLMO's corresponding to DLMO's.

character. This can be seen quite clearly for the CO molecule where the energy localization leads to single lone pair orbitals on the O atom and the density localization to trigonal ones. (See also the O-hybrids in CO and H<sub>2</sub>O.)

Quite remarkable is the similarity of the hybrids for the F-lone pair orbitals among the different localization methods and among the investigated molecules (In this case we can fortunately examine four molecules which is, if not sufficient, at least indicative.) This is not unexpected since they lie outside the bonding region and are consequently affected least by the atoms to which the F atom is bound. These data speak favourably for the transferability of LMO's.

The examination of the hybrids leading to the bond orbitals reveals some reasonable trends too (Table 15). As observed for the hybrids leading to lone pair orbitals we see here too that with increasing atomic number the *2p* character of the hybrids for the bond orbitals increases. This has been anticipated and qualitatively discussed for the C<sub>2</sub>H<sub>2</sub> and N<sub>2</sub> molecules by Hall and Lennard-Jones [19].

The more polar the bond becomes in a molecule involving one fixed atom the greater is the reduction in *s*-character of the hybrids for the less electronegative atom and the greater is the increase in *s*-character for the more electronegative atom. The more electronegative atom tends to attract the charge around its own nucleus, the *s*-character of its hybrids contributed to the bond orbital must therefore increase. We see this clearly from the series: Li<sub>2</sub> → LiH → LiF, B<sub>2</sub> → BF, F<sub>2</sub> → HF, BF → LiF, and C<sub>2</sub>H<sub>2</sub> → CO.

The agreement among the results of the four localization methods in Tables 14 and 15 is satisfactory in general, but in a few cases (where one could expect a better agreement because the qualitative structure of the LMO's is the same) it is only fair. In the larger fraction of the molecules it is the Magnasco-Perico method which gives the greatest differences, but there are also some molecules where the agreement among all methods is only fair.

## 5. Discussion and Conclusions

We summarize the results and attempt an explanation. The density localization method which we have introduced in these three publications has been established as a useful new intrinsic localization method. This method adds information to our knowledge about localized orbitals in atoms and molecules and helps us to understand the concept of localization itself. The concept of localized orbitals has been proved in many publications to be of great usefulness and it allows to bridge the gap between the qualitative chemical concepts on the one hand and the quantitative Hartree-Fock theory on the other hand. The classical chemical concepts can be reproduced in the quantum mechanical description of molecules by wavefunctions.

Because there are many different localization methods it could well be that they yield somewhat different types of LMO's. Greater differences are improbable and would in fact be quite embarrassing, but smaller differences are possible because we are dealing with external methods and intrinsic methods based on different separation functions for orbital separation [11]. It is thus gratifying that for the greater part of the molecules, which we have examined so far, the four localization

methods under investigation give the same qualitative answer and even a satisfactory or good quantitative agreement. There are, however, a few exceptions and they offer additional insight into the concept of localized orbitals. (It seems, though, that such problems as unconventional orbital structures arise mainly in diatomic molecules [4, 15, 17] and it is quite probable that for polyatomic molecules there will be no or only few qualitative differences among the localization methods, except that the arbitrariness of the external methods will play a greater role.) There is the  $C_2$  molecule which presents some difficulties. We have discussed this problem in II. One might expect a lone pair on each C atom and a double bond. This would result from the Magnasco-Perico method by not mixing the orbitals of  $\sigma$ - and  $\pi$ -symmetry. But then the  $CC'$  double bond would be a pure  $\pi$ -bond – a rather peculiar answer. Besides that the energy, the density, and the Boys localization methods do not support it. There is furthermore the LiF molecule, for which both the triple and the single bond seems to be a possible solution. On the assumption of an ionic model for this molecule this result can be explained. But the results for the BN and CO molecules are more difficult to rationalize. One can argue about the meaning of such results. They may arise from a certain arbitrariness of the localized orbitals (which does not preclude the usefulness of the results). But one can argue as well that they reflect details of the molecular electronic structure. One could also extract chemical information from some such results. (This might work in some cases and fail in others.) Let us take only one example which we considered already in II. (See also Ref. [19]  $NH_3$  will accept a proton to form  $NH_4^+$ . The N-lone pair orbital will become a bond orbital. The N atoms in  $N_2$  have lone pairs of electrons too, but  $N_2$  will not accept a proton. If we consider the detailed structure of these lone pair orbitals, this fact is understandable. The lone pair orbital in  $N_2$  is close to a  $2s$  atomic orbital, whereas the lone pair orbital in  $NH_3$  has a large extension in the direction away from the H atoms by making heavy use of the  $2p$  functions. LMO's and bonds are a breakdown of the total electronic density into components, which might be very useful. (E.g. for the transfer of LMO's between molecules, the calculation of correlation effects, or to extract some chemical information which might be more difficult to get otherwise.) We have stressed this point before. LMO's are not observables of any one state of any one system, but, as Ruedenberg *et al.* [10] have pointed out, "properties of individual orbitals can nonetheless be related to differences in expectation values of different states or different systems."

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