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Density Localization of Atomic and Molecular Orbitals

II. Homonuclear Diatomic Molecules

W. von Niessen

Max-Planck-Institut für Physik und Astrophysik, 8 München 23, Germany

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The density localization method previously described is applied to the homonuclear diatomic molecules Li_2, Be_2, B_2, C_2, N_2, and F_2. The method is based on the minimization of the sum of the interorbital density overlap integrals. The results of the density localization method are compared with the results of the energy localization method of Edmiston and Ruedenberg and with the results of the localization procedures of Boys and of Magnasco and Perico. The agreement among the four methods is in general good. With one exception we obtain also agreement with the classical chemical concepts of electron pairs.

Die Dichtelokalisierungsmethode, die in einer früheren Arbeit beschrieben worden ist, wird auf die homonuklearen zweiatomigen Moleküle Li_2, Be_2, B_2, C_2, N_2 und F_2 angewandt. Die Methode beruht auf der Minimierung der Summe der Dichteüberlappungsintegrale zwischen verschiedenen Orbitalen. Die Ergebnisse der Dichtelokalisierungsmethode werden mit den Resultaten der Energielokalisierungsmethode von Edmiston und Ruedenberg sowie mit denen der Lokalisierungsverfahren von Boys und von Magnasco und Perico verglichen. Die Übereinstimmung der Ergebnisse ist im allgemeinen gut. Mit einer Ausnahme entsprechen sie den klassisch-chemischen Vorstellungen.

1. Introduction

In a previous paper [1] – we refer to it as I – we have introduced the density localization method as an intrinsic localization method for atomic and molecular orbitals. With this approach we took up an earlier suggestion of Edmiston und Ruedenberg [2, 3]. The density localized molecular orbitals are defined to be those orbitals which minimize the sum of the interorbital density overlap integrals. In I we have presented the application of the density localization method to the two atoms Be and Ne. We now apply the method to the homonuclear diatomic molecules Li_2, Be_2, B_2, C_2, N_2, and F_2. The results are compared with those of the energy localization method of Edmiston and Ruedenberg [2, 4], and of the localization procedures of Boys [5, 6] and of Magnasco and Perico [7]. The aim has been to investigate the general qualitative and quantitative agreement among these four localization methods and in particular the similarity between the energy and the density localized molecular orbitals (ELMO's, DLMO's) expected because of the physical relation between exchange interaction and density overlap. For all molecules listed above we obtain agreement among the results of the four localization methods and with the chemical concepts except for the C_2 molecule. The quantitative numerical agreement among the four methods is in general quite good. In some cases the results of the method of Magnasco and Perico show greater deviations, but no general trend can be established.

In Section 2 we give a description of the density localization method, and in Section 3 a short outline of the three other localization methods applied. Some computational aspects will be considered in Section 4 and the calculations are discussed in Section 5.

2. Outline of the Density Localization Method

We are restricting our considerations to the case of a one-determinantal approximation to a wavefunction with doubly filled orthonormal orbitals as for example determined by a SCF calculation. For a $2n$ electron system the wavefunction $|\Psi\rangle$ may be written as (for the notation see I)

$$|\Psi\rangle = (2n!)^{1/2}\,\mathscr{A}\{|1+\rangle|1-\rangle \ldots |n+\rangle|n-\rangle\}\,, \tag{1}$$

where $\mathscr{A}$ is the antisymmetric projection operator with $\mathscr{A}^2 = \mathscr{A}$. The row matrix of molecular orbitals (MO's):

$$\underline{|\Phi\rangle} := (|1\rangle, \ldots, |i\rangle, \ldots, |n\rangle)\,, \tag{2}$$

can be subjected to a unitary transformation without changing the wavefunction $|\Psi\rangle$ itself. The density localized atomic and molecular orbitals are defined as those orbitals resulting from the unitary transformation which minimizes the sum of all density overlap integrals between the orbitals:

$$D = \sum_{i<j} [i^2 j^2] = \min\,, \tag{3}$$

where the density overlap between orbitals $|i\rangle$ and $|j\rangle$ is defined by

$$[i^2 j^2] := \int |\langle \boldsymbol{r}|i\rangle|^2\, |\langle \boldsymbol{r}|j\rangle|^2\, d^3\boldsymbol{r}$$

and the charge density of some orbital $|i\rangle$ is given by $|\langle \boldsymbol{r}|i\rangle|^2$. It is to be noted that the quantity $\sum_{i,j} [i^2 j^2]$ is invariant under unitary transformations, whereas the terms $\sum_i [i^4]$ and $\sum_{i \neq j} [i^2 j^2]$, into which it can be decomposed, are not invariant. Minimization of D is equivalent to maximization of $\sum_i [i^4]$, which is the sum of the self-overlaps of the charge densities.

The localization is done via a sequence of pairwise rotations of the orbitals in the vector space spanned by them which are chosen such that the maximum decrease in D is obtained. Convergence to the DLMO's is reached if for all pairs of orbitals $|i\rangle$, $|j\rangle$ the following conditions hold:

$$[i^3 j] - [i j^3] = 0 \tag{5}$$

with

$$[ijkl] := \int \langle i|\boldsymbol{r}\rangle \langle \boldsymbol{r}|j\rangle \langle k|\boldsymbol{r}\rangle \langle \boldsymbol{r}|l\rangle\, d^3\boldsymbol{r}\,. \tag{6}$$

Numerically it may be more convenient to test the decrease in D directly. Convergence is reached, if any further decrease in D is smaller than a given threshold.

3. Energy, Boys, and Magnasco-Perico Localization Methods

Because the results of the density localization method will be compared to those of the energy localization method, the Boys, and the Magnasco-Perico localization method, the bases of these methods are briefly described in this section. For a more detailed discussion we refer to the original literature. In the energy localization method of Edmiston and Ruedenberg [2, 4], which is based on an earlier suggestion of Lennard-Jones and Pople [8], the sum of the orbital self-interaction energies is maximized and thus the sum of the exchange and Coulomb energies between the orbitals minimized. The electron interaction energy

$$E = 2\sum_{i,j} [i^2 | j^2] - \sum_{i,j} [ij | ij] \tag{7}$$

consists of two terms, the Coulomb and exchange energy, which are separately invariant under unitary transformations. This is not the case for the term $D = \sum_i [i^2 | i^2]$ occurring in both energy terms. Maximization of D, which is the orbital self-interaction energy, defines the ELMO's. Maximization of D implies the minimization of the terms

$$2 \sum_{i \neq j} [i^2 | j^2] \quad \text{and} \quad \sum_{i \neq j} [ij | ij] \tag{8}$$

which are the Coulomb and exchange energies between the orbitals. This fact is important for the physical interpretation.

The method of Boys [5, 6] consists in maximizing the sum of the squares of the distances between the charge centroids of the orbitals

$$D = \sum_{i,j} [\langle i | \boldsymbol{r} | i \rangle - \langle j | \boldsymbol{r} | j \rangle]^2 . \tag{9}$$

This has been shown by Boys to be equivalent to the minimization of

$$I = \sum_i \langle ii | r_{12}^2 | ii \rangle \tag{10}$$

which Boys calls the sum of the quadratic repulsions of the orbitals with themselves [6]. The first formula is more convenient for computations because then only the $3n^2$ dipole moment matrix elements are required.

In the procedure of Magnasco and Perico [7] one starts with the definition of local electron populations for each MO. They have to be localized around atoms or between pairs of atoms, forming inner shells and lone pairs of electrons and bonds. This makes necessary a concept of the orbital structure prior to localization. For each orbital a local electron population is defined

$$P_i := \sum_{p,q \in \Gamma_i} c_{pi} c_{qi} \langle p | q \rangle , \tag{11}$$

where Γ_i denotes the set of functions contributing to this population. By maximizing the expression

$$P = \sum_i P_i \tag{12}$$

the uniformly localized orbitals of Magnasco and Perico (MPLMO's) are obtained. The arbitrariness of the method is contained in the definition of the sets Γ_i. It is an external method.

4. Computational Aspects

In I we have commented qualitatively on the computational aspects of the energy and the density localization method. We would like to come back to this point and compare the computational expense of all four localization methods under investigation. The two-electron integrals required for the energy localization procedure are in general available from the SCF calculation, but they have to be transformed to the basis of the occupied molecular orbitals. For the density localization method the basic density overlap integrals have to be computed and then transformed to the basis of the molecular orbitals. The calculation of these basic integrals as well as their transformation is significantly simplified by the high degeneracy of these integrals compared to the two-electron energy integrals. They are invariant with respect to any permutation of the four indices. It turned out that for the energy localization method the basis transformation of the integrals is computationally dominant in the cases considered. For the density localization procedure the dominant part is the calculation of the basic integrals. Comparing the calculation times of the energy, density, Boys, and Magnasco-Perico localization methods we find that the first two use large amounts of computer time, because the computation time is proportional to at least the fifth power of the number of basis functions. Which of the two methods, the energy or the density localization method, is faster cannot be stated in general. For small systems the energy localization method seems to be faster while for larger systems the density localization method becomes more and more favourable. The computation time of the Boys and the Magnasco-Perico localization method is proportional to the second power of the number of basis functions. The two methods are thus very fast and require few seconds of computer time on an IBM 360/91 computer for the largest molecules examined. For basis sets of 9*s*-type and 5*p*-type Gaussian lobe functions contracted to 5*s*-type and 3*p*-type functions for the second row atoms and of 4*s*-type functions for the H atom (contracted to 2*s*-type functions) some typical computation times are given in Table 1.

To investigate the sensitivity of the LMO's to a change in the wavefunction and to a different choice of starting point in the numerical process of localization the C_2 and N_2 molecules were examined in more detail. For C_2 ($1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4, {}^1\Sigma_g^+$) Edmiston and Ruedenberg [9] analyzing the wavefunction of Ransil [10] did not find equivalent orbitals as LMO's. We have calculated a fair

Table 1. Typical computation times in minutes for the energy and the density localization method[a]

Molecule	Energy localization method	Density localization method
C_2	1.4	3.7
N_2	2.2	3.8
F_2	5.2	4.4
HF	0.13	0.5
H_2O	0.4	0.7
NH_3	1.05	1.1
CH_4	1.9	1.5

[a] The numbers refer to an IBM 360/91 computer.

number of wavefunctions for this molecule with basis sets of type (5/1), (5/2), (7/3), and (9/5) with different contractions [11–14]. From our results we can draw the following conclusions. For a given wavefunction and a given localization method only one set of LMO's is obtained as solution, but if different wavefunctions are examined by the same localization method sets of LMO's differing qualitatively can be obtained. This was found for the density and the Boys localization method; for the Edmiston-Ruedenberg localization method on the other hand the solutions were always of the same type.

For the N_2 molecule a number of wavefunctions were calculated using the same basis sets as described for C_2. In all cases the methods of Edmiston and Ruedenberg and of Boys gave the same results, but we had some difficulties when applying the density localization method. For internuclear separations larger than 2.3 a.u. the answer was unique: trigonally equivalent banana bond orbitals resulted. But at the experimental distance of 2.0693 a.u. some wavefunctions gave distorted bond orbitals as solutions. The reason for this sensitivity of the density localization method might be the tight bonding structure of N_2 and the short range character of the δ-function potential which is the basis of this method. Aside from these two cases no indications for different sets of LMO's as solutions were found with other molecules. However, a further example will be discussed in another context [15].

To examine the existence of multiple extrema, we took different starting points for the localization. In all cases investigated convergence to the same solution was achieved. This does not disprove the existence of multiple extrema, we only did not find any.

5. The Calculations

Programs have been written to calculate SCF wavefunctions and from these the energy, density, Boys, and Magnasco-Perico localized molecular orbitals. We present here the results for the homonuclear diatomic molecules Li_2, Be_2, B_2, C_2, N_2, and F_2. The basis functions used are the Gaussian lobe functions. For all atoms except the H atom 9 functions of s-type are used, the 5 with the largest exponents being contracted into one group. For the H atom 4 functions of s-type are used, the two with the largest exponents contracted into one group. The exponents and contraction coefficients are taken from Huzinaga's paper [13]. For the Li and Be atom 2 functions of p-type are used. The exponents η and the distance R from the center are for Li: $\eta_1 = 0.5$, $R_1 = \pm 0.075$ a.u., $\eta_2 = 2.0$, $R_2 = \pm 0.065$ a.u. and for Be: $\eta_1 = 0.6$, $R_1 = \pm 0.07$ a.u., $\eta_2 = 2.4$, $R_2 = \pm 0.06$ a.u. For the atoms from B to F 5 functions of p-type are used, the three with the largest exponents contracted to one group with exponents and contraction coefficients as given by Whitten [14].

The results we obtained for the LMO's of these molecules agree qualitatively with the results given by Edmiston and Ruedenberg [4, 9] except for the C_2 molecule. We are going to discuss this case in detail below. The following conclusions can be drawn from a comparison of the different localized orbitals: The numerical agreement is very satisfactory in general among the results of the intrinsic methods. The best agreement is found between the LMO's of the energy and the Boys localization methods. The agreement between the ELMO's and DLMO's is nearly as good. The more "important" coefficients ($c \geqq 0.1$) in the expansion of the LMO's often agree to two and sometimes three significant figures, which is quite satisfactory in view of the fact that different separation functions are used in these three methods. The results of the Magnasco-Perico procedure show greater deviations, although there is good agreement with the results of the other methods in some cases. It is difficult to understand why the agreement is good in some cases and only fair in others. The *s*-type Gaussian functions with small exponents give the largest contribution to the inner shell LMO's of the heavy atoms in the case of the MPLMO's and smaller contributions in the case of the DLMO's, ELMO's, and the LMO's of Boys (BLMO's). If equivalent orbitals are found for a molecule the equivalence is in general numerically best fulfilled for the BLMO's and the MPLMO's and is not so good for the DLMO's and the ELMO's. The reason might be the insensitivity (to a variation in the LMO's) of the potential used as the separation function and the amount of numerical processes involved.

It has been stated in the literature [7, 16] that for molecules containing lone pairs of electrons the MPLMO's have a larger $2p$-contribution in the lone pair orbitals than do the ELMO's and that the reverse is true for the bond orbitals. We have examined a fairly large number of molecules, some of which have not been analyzed from this point of view so far, and our results are not in complete agreement with this statement. In Table 2 we give the local $2p$-type populations for several atoms for the lone pair and bond orbitals obtained by the energy, density, Boys, and Magnasco-Perico localization method. We have added the results for a number of other molecules which we shall discuss in more detail in a subsequent paper [15]. In most cases the BLMO's have about the same $2p$-contribution as the ELMO's. But apparently no general statement can be made about the $2p$-contribution to the MPLMO's compared to the ELMO's. For the atoms F in F_2, F in LiF, B in BF, N in NH_3, and O in H_2O the MPLMO's exhibit a larger $2p$-contribution in the lone pair orbital (and a smaller $2p$-contribution in the bond orbital) than do the ELMO's in agreement with previous work. The

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

	Bond orbital				Lone pair orbital			
Atom	ELMO	DLMO	BLMO	MPLMO	ELMO	DLMO	BLMO	MPLMO
B in B_2	0.1973	0.2045	0.1904	0.2492	0.2067	0.2006	0.2122	0.1673
N in N_2	0.3046	0.3119	0.2997	0.3362	0.2618	0.2417	0.2735	0.1883
F in F_2	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_3	0.3303	0.3316	0.3280	0.2999	0.7026	0.6982	0.7095	0.7912
O in H_2O	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

Table 3. Bond distances (*R*) and total SCF energies (*E*)

Molecule	*R* [a.u.]	*E* [a.u.]
Li_2	5.0504	− 14.8626115
Be_2	3.78	− 29.0862513
B_2	3.0028	− 49.0324955
C_2	2.4788	− 75.3576030
N_2	2.0693	− 108.8862996
F_2	2.6791	− 198.7058343

reverse is true for B in B_2, N in N_2, N in BN, F in BF, C in CO, O in CO, and F in HF. It seems also that there is a dependence on the wavefunction.

The results for the individual molecules are discussed in more detail in the following. Table 3 contains information about the geometry and the total energies obtained. Because of the length of the Gaussian function expansions of the orbitals we do not give them here. Instead only the transformation matrices from the canonical MO's (CMO's) to the LMO's are given. This seems to be the most useful information, because, as Edmiston and Ruedenberg [4] stated, the transformation matrices are approximately independent of the size of the basis set used to approximate the wavefunction. The signs of the CMO's are chosen in the following way: The largest coefficient of an *s*-type function in the expansion of a particular CMO or of a $2p\pi$-type function is given the positive sign. If there are two coefficients of equal magnitude and opposite sign, the first one carries the positive sign. In cases of degeneracy or of wavefunctions differing considerably in the basis set size this might not be sufficient, but this choice of the signs should eliminate the major uncertainties [17]. The transformation matrices for the four localization methods are given in Tables 4–10 for the different molecules.

Table 4. Transformation matrices for Li_2

ENERGY LOCALIZATION

	iLi	iLi'	bσLiLi'
$1\sigma_g$	0.70373	0.70373	0.09763
$1\sigma_u$	0.70711	-0.70711	0.00000
$2\sigma_g$	-0.06903	-0.06903	0.99522

DENSITY LOCALIZATION

	iLi	iLi'	bσLiLi'
$1\sigma_g$	0.69921	0.69921	0.14908
$1\sigma_u$	0.70711	-0.70711	0.0
$2\sigma_g$	-0.10541	-0.10541	0.98883

BOYS LOCALIZATION

	iLi	iLi'	bσLiLi'
$1\sigma_g$	0.70705	0.70705	0.01264
$1\sigma_u$	0.70711	-0.70711	0.0
$2\sigma_g$	-0.00893	-0.00893	0.99992

MAGNASCO-PERICO LOCALIZATION

	iLi	iLi'	bσLiLi'
$1\sigma_g$	0.68976	0.68976	0.22013
$1\sigma_u$	0.70711	-0.70711	0.0
$2\sigma_g$	-0.15565	-0.15565	0.97547

The LMO's resulting from the Magnasco-Perico localization method cannot be directly compared to the other LMO's, because orbitals of σ- and π-type symmetry are not mixed. Therefore a unitary transformation [7] has been applied after the localization.

Li_2 (Table 4)

Localization yields an inner shell on each Li atom and a bond orbital connecting the two atoms (Table 4). As mentioned previously the most important change in the localization functions results from the combination of the $1\sigma_g$ and $1\sigma_u$ orbitals. The exchange integrals change by about a factor of 200 and the density overlap integrals by about a factor of 400. Similar figures apply to all homonuclear diatomic molecules. The transformation matrices are nearly an identity with respect to the bond orbital.

Be_2 (Table 5)

Be_2 is a "nonbonded molecule". Consequently we obtain by localization an inner and an outer shell on each Be atom. The localization consists essentially in a left-right combination of $1\sigma_g$ and $1\sigma_u$ on the one hand and of $2\sigma_g$ and $2\sigma_u$ on the other hand, as indicated by the transformation matrices (Table 5). Because of the arbitrariness in the choice of the local electron populations in the Magnasco-Perico method a starting point can be selected that gives rise to two bonds as LMO's. This is perhaps the simplest example of forcing an unreasonable result. But it should be mentioned that in other cases (LiF e.g.) this method is fairly independent of the initial choice of the local electron populations.

Table 5. Transformation matrices for Be_2

ENERGY LOCALIZATION

	iBe	iBe'	ℓσBe	ℓσBe'
$1\sigma_g$	0.70160	0.70160	0.08809	0.08809
$1\sigma_u$	0.70332	-0.70332	0.07314	-0.07312
$2\sigma_g$	-0.08810	-0.08808	0.70160	0.70160
$2\sigma_u$	-0.07313	0.07312	0.70331	-0.70332

DENSITY LOCALIZATION

	iBe	iBe'	ℓσBe	ℓσBe'
$1\sigma_g$	0.69564	0.69564	0.12685	0.12685
$1\sigma_u$	0.69900	-0.69900	0.10679	-0.10679
$2\sigma_g$	-0.12685	-0.12685	0.69564	0.69564
$2\sigma_u$	-0.10679	0.10679	0.69900	-0.69900

BOYS LOCALIZATION

	iBe	iBe'	ℓσBe	ℓσBe'
$1\sigma_g$	0.70708	0.70708	-0.00668	-0.00668
$1\sigma_u$	0.70680	-0.70680	-0.02090	0.02090
$2\sigma_g$	0.00668	0.00668	0.70708	0.70708
$2\sigma_u$	0.02090	-0.02090	0.70680	-0.70680

MAGNASCO-PERICO LOCALIZATION

	iBe	iBe'	ℓσBe	ℓσBe'
$1\sigma_g$	0.68188	0.68188	0.18719	0.18719
$1\sigma_u$	0.69619	-0.69619	0.12377	-0.12377
$2\sigma_g$	-0.18719	-0.18719	0.68188	0.68188
$2\sigma_u$	-0.12377	0.12377	0.69619	-0.69619

Table 6. Transformation matrices for B_2

ENERGY LOCALIZATION	iB	iB'	bσBB'	ℓσB	ℓσB'
$1\sigma_g$	0.70099	0.70099	0.10140	0.05893	0.05893
$1\sigma_u$	0.70299	-0.70299	-0.00000	0.07616	-0.07616
$2\sigma_g$	-0.08852	-0.08853	0.92124	0.26043	0.26043
$2\sigma_u$	-0.07616	0.07616	0.00000	0.70299	-0.70300
$3\sigma_g$	-0.02788	-0.02788	-0.37555	0.65476	0.65475
DENSITY LOCALIZATION	iB	iB'	bσBB'	ℓσB	ℓσB'
$1\sigma_g$	0.69481	0.69481	0.14307	0.08370	0.08370
$1\sigma_u$	0.69803	-0.69803	0.0	0.11292	-0.11292
$2\sigma_g$	-0.12586	-0.12586	0.90735	0.26929	0.26929
$2\sigma_u$	-0.11292	0.11292	0.0	0.69803	-0.69803
$3\sigma_g$	-0.03742	-0.03742	-0.39528	0.64844	0.64844
BOYS LOCALIZATION	iB	iB'	bσBB'	ℓσB	ℓσB'
$1\sigma_g$	0.70511	0.70511	0.05860	0.03312	0.03312
$1\sigma_u$	0.70611	-0.70611	0.0	0.03744	-0.03744
$2\sigma_g$	-0.05053	-0.05053	0.93204	0.25120	0.25120
$2\sigma_u$	-0.03744	0.03744	0.0	0.70611	-0.70611
$3\sigma_g$	-0.01615	-0.01615	-0.35760	0.66015	0.66015
MAGNASCO-PERICO LOCALIZATION	iB	iB'	bσBB'	ℓσB	ℓσB'
$1\sigma_g$	0.68728	0.68728	0.14354	0.13171	0.13171
$1\sigma_u$	0.69347	-0.69347	0.0	0.13821	-0.13821
$2\sigma_g$	-0.15317	-0.15317	0.85477	0.33350	0.33350
$2\sigma_u$	-0.13821	0.13821	0.0	0.69347	-0.69347
$3\sigma_g$	-0.06471	-0.06471	-0.49877	0.60945	0.60945

B_2 (Table 6)

For the B_2 molecule the electronic configuration $1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 3\sigma_g^2, {}^1\Sigma_g^+$ was analyzed. After localization we find an inner shell and a lone pair orbital on each B atom and a bond orbital linking the two atoms (Table 6). This lone pair orbital has a marked *s*-type contribution, which is largest for the Magnasco-Perico LMO's and decreases for the energy, the Boys and the density localized orbitals in the given order.

C_2 (Tables 7, 8)

According to the literature [9] the MO's of C_2 wavefunctions are difficult to localize. The conclusions reached here are the following: The energy localization method gave rise to effectively no problems, only one set of LMO's resulted. The density localization method gave two different solutions depending on the wavefunction examined. The method of Boys yielded two different solutions in most cases too, but sometimes did not converge and gave non-equivalent orbitals as intermediate solution. The method of Magnasco and Perico lead to easy convergence. A number of wavefunctions was examined for the C_2 molecule in the electronic configuration $1\sigma_g^2\, 1\sigma_u^2\, 2\sigma_g^2\, 2\sigma_u^2\, 1\pi_u^4, {}^1\Sigma_g^+$ using basis sets of type (5/1), (5/2), (7/3), and (9/5) with different contraction coefficients and different parameters for the *p*-type functions [11–14]. We give representative results of our investigations without specifying the wavefunctions in detail [17]. For all wave-

Table 7. Transformation matrices for C_2

ENERGY LOCALIZATION

	iC	iC'	b1CC'	b2CC'	b3CC'	b4CC'
$1\sigma_g$	0.70074	0.70090	0.06650	0.06650	0.06655	0.06649
$1\sigma_u$	0.70223	-0.70207	0.05908	0.05910	-0.05901	-0.05914
$2\sigma_g$	-0.09405	-0.09407	0.49558	0.49545	0.49583	0.49537
$2\sigma_u$	-0.08356	0.08355	0.49643	0.49665	-0.49587	-0.49704
$1\pi_u$	-0.00001	-0.00001	-0.70675	0.70664	0.02423	-0.02398
	0.00001	0.00000	0.02353	-0.02469	0.70694	-0.70645

DENSITY LOCALIZATION A

	iC	iC'	b1CC'	b2CC'	b3CC'	b4CC'
$1\sigma_g$	0.69267	0.69267	0.10051	0.10052	0.10048	0.10050
$1\sigma_u$	0.69383	-0.69383	0.09646	0.09642	-0.09649	-0.09644
$2\sigma_g$	-0.14214	-0.14214	0.48982	0.48989	0.48970	0.48977
$2\sigma_u$	-0.13640	0.13640	0.49067	0.49042	-0.49079	-0.49055
$1\pi_u$	0.0	0.00000	-0.51834	0.51829	-0.48103	0.48094
	0.0	0.0	0.48086	-0.48111	-0.51820	0.51844

DENSITY LOCALIZATION B

	iC	iC'	b1CC'	b2CC'	b3CC'	b4CC'
$1\sigma_g$	0.69398	0.69414	0.01992	0.02005	0.13376	0.13368
$1\sigma_u$	0.69635	-0.69620	0.12332	-0.12328	0.00010	0.00002
$2\sigma_g$	-0.13520	-0.13520	0.10223	0.10276	0.68665	0.68626
$2\sigma_u$	-0.12330	0.12330	0.69635	-0.69620	0.00047	0.00004
$1\pi_u$	-0.00002	-0.00002	0.69920	0.69928	-0.09168	-0.11714
	0.00000	0.00000	-0.01284	-0.01241	0.70868	-0.70531

BOYS LOCALIZATION A

	iC	iC'	b1CC'	b2CC'	b3CC'	b4CC'
$1\sigma_g$	0.70621	0.70532	0.01273	0.03476	0.03476	0.03473
$1\sigma_u$	0.70737	-0.70648	0.00553	-0.01273	-0.01271	-0.01263
$2\sigma_g$	-0.02964	-0.05113	0.55539	0.47904	0.47899	0.47869
$2\sigma_u$	0.00428	0.02806	0.83147	-0.32156	-0.32109	-0.31834
$1\pi_u$	0.00005	0.00001	0.00188	0.58761	0.19496	-0.78530
	-0.00001	-0.00000	-0.00028	0.56609	-0.79252	0.22683

BOYS LOCALIZATION B

	iC	iC'	b1CC'	b2CC'	b3CC'	b4CC'
$1\sigma_g$	0.70445	0.70452	0.04623	0.04621	0.03953	0.03953
$1\sigma_u$	0.70622	-0.70616	0.03595	-0.03594	0.00003	0.00003
$2\sigma_g$	-0.06071	-0.06068	0.56349	0.56357	0.42279	0.42279
$2\sigma_u$	-0.03596	0.03593	0.70597	-0.70642	0.00037	0.00037
$1\pi_u$	0.00315	0.00316	0.34683	0.34612	-0.87013	-0.05258
	0.00223	0.00224	0.24572	0.24522	0.25012	-0.90384

functions examined the energy localization method gave one set of LMO's as solution (the transformation matrix for the wavefunction calculated with the (9/5) basis set is listed in Table 7). These ELMO's are equivalent orbitals. The analysis of the C_2 wavefunction of Ransil [10] by Edmiston and Ruedenberg [9] did on the other hand not give equivalent orbitals of any kind. To describe the bonding orbitals which we have obtained (b1CC', b2CC', b3CC', and b4CC') their charge centroids are given in Table 8. These orbitals have the symmetry property expected of equivalent orbitals. Bond orbitals 1 and 2 are transformed into each other by a rotation through 180° about the CC' axis, so are orbitals 3 and 4. A rotation through 90° plus a reflection in the plane perpendicular to and bisecting the internuclear axis transforms 1 into 3 and 2 into 4 and vice versa. From the transformation matrix in Table 7 it follows that these orbitals arise roughly in the following way: left-right combination of $2\sigma_g$ and $2\sigma_u$ gives a $2s$-type atomic orbital on atoms C and C', combination of the $2s$ orbital on atom C with the π_x-canonical orbital gives orbitals 1 and 2 lying in the $x-z$-plane in the neighbourhood of one C atom. A similar combination of the $2s$ orbital on atom C' with the π_y canon-

Table 8. Charge centroids of the bonding orbitals in C_2 [a]

Orbital	Method	x	y	z
b1CC′	Energy	0.588	0.008	0.749
b2CC′		−0.588	−0.007	0.749
b3CC′		0.008	−0.589	1.730
b4CC′		−0.008	0.588	1.730
b1CC′	Density A	−0.003	0.574	0.679
b2CC′		0.003	−0.574	0.679
b3CC′		0.574	0.003	1.799
b4CC′		−0.574	−0.003	1.799
b1CC′	Density B	−0.121	−0.004	1.094
b2CC′		−0.121	−0.004	1.385
b3CC′		0.145	−0.816	1.239
b4CC′		0.097	0.823	1.239
b1CC′	Boys A	0.000	−0.002	0.356
b2CC′		−0.507	−0.418	1.535
b3CC′		0.616	−0.229	1.535
b4CC′		−0.109	0.648	1.532
b1CC′	Boys B	−0.373	−0.121	0.426
b2CC′		−0.372	−0.121	2.053
b3CC′		0.523	−0.345	1.239
b4CC′		0.222	0.586	1.239

[a] The molecule lies along the z-axis with one C atom in the origin the other at a z-value of 2.4788 a.u.

ical orbital gives orbitals 3 and 4 lying in the $y-z$-plane in the neighbourhood of the other C atom.

The same type of orbital is obtained by the density localization method for a wavefunction calculated with a (5/1) basis set. The transformation matrix is given as "Density Localization A" in Table 7 and the charge centroids of the bonding orbitals are given in Table 8. An analysis of the wavefunction resulting from the (9/5) basis set gave a different type of orbital which is presented as "Density Localization B" in Table 7 and 8. These orbitals form two sets of equivalent orbitals. Orbitals b1CC′ and b2CC′ lie quite close to the middle of the bond, one to the left, one to the right. Orbitals b3CC′ and b4CC′ have their charge centroids in the $x-y$-plane defined by the middle of the bond. Result *B* was found most frequently in the analysis of the different wavefunctions.

Applying the Boys localization method to a wavefunction calculated with a (7/3) basis set gave orbitals similar to type B described above. The results are given as "Boys Localization B" in Tables 7 and 8. Compared to the corresponding DLMO's the charge centroids of the orbitals b1CC′ and b2CC′ lie much closer to the C atoms. They appear to be mixtures of bond and lone pair orbitals. Localization of the MO's of a similar (7/3) wavefunction using slightly different parameters for the p-functions by the Boys method gave still a new set of LMO's, which are unsymmetric with respect to the two C atoms. All four orbitals are mixtures of lone pair and bonding orbitals. A single orbital is placed at one C atom and three trigonally equivalent orbitals are placed at the other C atom. There are two degenerate solutions of this type with the C atoms interchanged. We list one solution in Tables 7 and 8 ("Boys Localization A"). These two types of

Table 9. Transformation matrices for N_2

ENERGY LOCALIZATION

	iN	iN'	$\ell\sigma$N	$\ell\sigma$N'	bt1NN'	bt2NN'	bt3NN'
$1\sigma_g$	0.69991	0.69991	0.05983	0.05984	0.06615	0.06608	0.06596
$1\sigma_u$	0.70195	-0.70196	0.08523	-0.08523	-0.00001	0.00001	-0.00000
$2\sigma_g$	-0.09417	-0.09417	0.18904	0.18903	0.55172	0.55125	0.55002
$2\sigma_u$	-0.08522	0.08523	0.70194	-0.70196	0.00000	0.00000	-0.00001
$3\sigma_g$	-0.03547	-0.03548	0.67875	0.67873	-0.15976	-0.15942	-0.15866
$1\pi_u$	0.00001	0.00002	-0.00008	-0.00007	-0.67895	0.73228	-0.05281
	0.00000	0.00000	-0.00028	-0.00029	-0.45247	-0.36070	0.81558

DENSITY LOCALIZATION

	iN	iN'	$\ell\sigma$N	$\ell\sigma$N'	bt1NN'	bt2NN'	bt3NN'
$1\sigma_g$	0.69276	0.69276	0.07955	0.07956	0.09726	0.09679	0.09323
$1\sigma_u$	0.69650	-0.69650	0.12200	-0.12200	0.00000	-0.00000	0.00000
$2\sigma_g$	-0.13724	-0.13724	0.23031	0.23032	0.54423	0.54102	0.51706
$2\sigma_u$	-0.12200	0.12200	0.69650	-0.69650	0.00001	-0.00001	0.00001
$3\sigma_g$	-0.03541	-0.03541	0.66375	0.66374	-0.20646	-0.20323	-0.18015
$1\pi_u$	0.00000	0.00000	0.00070	0.00068	-0.61421	0.77229	-0.16221
	-0.00001	-0.00001	-0.00836	-0.00836	-0.52390	-0.24535	0.81559

BOYS LOCALIZATION

	iN	iN'	$\ell\sigma$N	$\ell\sigma$N'	bt1NN'	bt2NN'	bt3NN'
$1\sigma_g$	0.70440	0.70440	0.03408	0.03408	0.04207	0.04207	0.04207
$1\sigma_u$	0.70565	-0.70565	0.04531	-0.04531	0.0	0.0	-0.00000
$2\sigma_g$	-0.05810	-0.05810	0.16508	0.16508	0.55939	0.55939	0.55939
$2\sigma_u$	-0.04531	0.04531	0.70565	-0.70565	0.0	0.00000	0.0
$3\sigma_g$	-0.02099	-0.02099	0.68672	0.68672	-0.13655	-0.13655	-0.13655
$1\pi_u$	0.00000	0.0	0.0	0.0	-0.45401	-0.36071	0.81472
	0.0	0.0	0.0	0.00000	-0.67863	0.73250	-0.05387

MAGNASCO-PERICO LOCALIZATION

	iN	iN'	$\ell\sigma$N	$\ell\sigma$N'	bt1NN'	bt2NN'	bt3NN'
$1\sigma_g$	0.69123	0.69123	0.10911	0.10911	0.08283	0.08283	0.08283
$1\sigma_u$	0.69697	-0.69697	0.11929	-0.11929	0.0	0.0	0.0
$2\sigma_g$	-0.14224	-0.14224	0.34004	0.34004	0.49271	0.49271	0.49271
$2\sigma_u$	-0.11929	0.11929	0.69697	-0.69697	0.0	0.0	0.0
$3\sigma_g$	-0.04432	-0.04432	0.61030	0.61030	-0.28933	-0.28933	-0.28933
$1\pi_u$	0.0	0.0	0.0	0.0	-0.81650	0.40825	0.40825
	0.0	0.0	0.0	0.0	0.0	-0.70711	0.70711

orbitals are typical results of the Boys localization method, but other solutions are obtained too: orbitals of the type as described above but considerably distorted and nonequivalent orbitals. These were generally found if no satisfactory convergence in the localization process could be achieved. These results indicate that the hypersurface involved in the localization process is very flat in the neighbourhood of the extremum. (See also the discussion in Ref. [9].)

The orbitals resulting from the Magnasco-Perico localization are two inner shells, two 2*s* orbitals and two π-bonds. A mixing of the 2*s*- with the π-orbital is expected to give better localized orbitals (see above). However, it is not obvious which transformation has to be applied to give this result. The external character of the Magnasco-Perico method gives too great an arbitrariness in this case (see Section 3).

Finally two things should be noted. All types of LMO's which we have found for the C_2 molecule do not conform with the classical chemical concepts of electron pairs. Secondly different wavefunctions can give different sets of LMO's as solutions, but there is little indication of multiple extrema in the localization process, because in no case two different solutions have been obtained for a given wavefunction.

N_2 (Table 9)

All localization procedures yield an inner shell and a lone pair orbital on each atom and three trigonally equivalent banana bond orbitals linking the two atoms. (Table 9; the transformation matrix for the density localization method was obtained from a wavefunction calculated with a (7/3) basis set because the (9/5) wavefunction lead to somewhat distorted bond orbitals (we would like to note that N_2 wavefunctions calculated with Cartesian Gaussian functions as basis functions do not seem to show this distortion)). The lone pair orbitals have a large *s*-type contribution, although it is smaller than in the case of the B_2 molecule. If one compares the structure of these orbitals with the lone pair orbital in NH_3, which will be discussed in a subsequent paper, we find that for NH_3 the 2*p*-contribution is more than doubled. This gives rise to a much larger extension of the lone pair orbital away from the molecule. This can explain why NH_3 will easily accept a proton to form NH_4^+ whereas N_2 will not. The lone pair orbitals of N_2

Table 10. Transformation matrices for F_2

ENERGY LOCALIZATION

	iF	iF'	ℓt1F	ℓt2F	ℓt3F	ℓt1F'	ℓt2F'	ℓt3F'	bσFF'
$1\sigma_g$	0.69962	0.69963	0.05762	0.05762	0.05756	0.05763	0.05759	0.05757	0.03387
$1\sigma_u$	0.69917	-0.69917	0.06102	0.06101	0.06095	-0.06104	-0.06099	-0.06096	-0.00000
$2\sigma_g$	-0.09896	-0.09897	0.35389	0.35384	0.35350	0.35396	0.35368	0.35356	0.47919
$2\sigma_u$	-0.10565	0.10565	0.40385	0.40379	0.40335	-0.40398	-0.40360	-0.40343	-0.00001
$1\pi_u$	-0.00000	-0.00000	0.19395	0.37357	-0.56818	-0.45296	-0.08300	0.53660	-0.00001
	-0.00000	-0.00001	-0.54366	0.44008	0.10376	-0.35765	0.57140	-0.21352	-0.00003
$3\sigma_g$	-0.02705	-0.02705	0.19561	0.19559	0.19528	0.19571	0.19545	0.19532	-0.87706
$1\pi_g$	0.00001	0.00000	0.28921	0.28769	-0.57757	0.38069	0.18512	-0.56640	0.00012
	0.00000	0.00000	-0.49954	0.50046	-0.00085	0.43377	-0.54692	0.11279	0.00004

DENSITY LOCALIZATION

	iF	iF'	ℓt1F	ℓt2F	ℓt3F	ℓt1F'	ℓt2F'	ℓt3F'	bσFF'
$1\sigma_g$	0.69307	0.69308	0.07935	0.07915	0.07905	0.07933	0.07921	0.07902	0.04095
$1\sigma_u$	0.69172	-0.69171	0.08490	0.08468	0.08456	-0.08487	-0.08474	-0.08453	0.00000
$2\sigma_g$	-0.13612	-0.13612	0.36071	0.35988	0.35945	0.36059	0.36013	0.35933	0.43045
$2\sigma_u$	-0.14673	0.14673	0.40025	0.39919	0.39864	-0.40010	-0.39950	-0.39848	-0.00000
$1\pi_u$	0.00000	0.00000	0.50507	-0.49474	-0.01171	0.52641	-0.46841	-0.05897	0.00031
	0.00000	0.00000	0.27835	0.29784	-0.57777	0.23578	0.33735	-0.57499	0.00045
$3\sigma_g$	-0.03350	-0.03350	0.17613	0.17533	0.17492	0.17602	0.17556	0.17480	-0.90169
$1\pi_g$	0.00000	-0.00000	0.44630	-0.54050	0.09313	-0.47501	0.52176	-0.04616	0.00006
	0.00000	-0.00000	0.36525	0.20332	-0.57032	-0.32723	-0.24694	0.57614	-0.00003

BOYS LOCALIZATION

	iF	iF'	ℓt1F	ℓt2F	ℓt3F	ℓt1F'	ℓt2F'	ℓt3F'	bσFF'
$1\sigma_g$	0.70392	0.70393	0.03718	0.03718	0.03718	0.03718	0.03718	0.03718	0.02613
$1\sigma_u$	0.70388	-0.70387	0.03901	0.03901	0.03901	-0.03901	-0.03901	-0.03901	0.00000
$2\sigma_g$	-0.06350	-0.06350	0.33444	0.33444	0.33444	0.33444	0.33444	0.33444	0.56641
$2\sigma_u$	-0.06757	0.06757	0.40638	0.40638	0.40638	-0.40638	-0.40638	-0.40638	0.0
$1\pi_u$	0.00000	-0.00000	-0.39192	0.56311	-0.17119	-0.10676	0.54476	-0.43800	0.0
	0.0	0.00000	0.42395	0.12744	-0.55139	-0.56739	0.19124	0.37616	0.00000
$3\sigma_g$	-0.02134	-0.02134	0.23116	0.23116	0.23116	0.23116	0.23116	0.23116	-0.82371
$1\pi_g$	0.00000	0.0	-0.46223	0.53071	-0.06849	0.00223	-0.50111	0.49888	0.00000
	0.0	0.0	0.34595	0.22732	-0.57327	0.57735	-0.28674	-0.29060	0.0

MAGNASCO-PERICO LOCALIZATION

	iF	iF'	ℓt1F	ℓt2F	ℓt3F	ℓt1F'	ℓt2F'	ℓt3F'	bσFF'
$1\sigma_g$	0.68277	0.68278	0.10343	0.10343	0.10343	0.10343	0.10343	0.10343	0.05866
$1\sigma_u$	0.68263	-0.68262	0.10650	0.10650	0.10650	-0.10650	-0.10650	-0.10650	0.00000
$2\sigma_g$	-0.17553	-0.17553	0.33913	0.33913	0.33913	0.33913	0.33913	0.33913	0.49833
$2\sigma_u$	-0.18447	0.18447	0.39411	0.39411	0.39411	-0.39411	-0.39411	-0.39411	0.00000
$1\pi_u$	0.0	0.0	0.40765	0.15025	-0.55790	-0.47496	-0.04680	0.52175	0.0
	0.0	0.0	-0.40885	0.55746	-0.14861	-0.32825	0.57545	-0.24720	0.0
$3\sigma_g$	-0.05482	-0.05482	0.20239	0.20239	0.20239	0.20239	0.20239	0.20239	-0.86500
$1\pi_g$	0.0	0.0	0.47496	0.04680	-0.52175	0.40765	0.15025	-0.55790	0.0
	0.0	0.0	-0.32825	0.57545	-0.24720	0.40885	-0.55746	0.14861	0.0

are close to 2*s*-atomic orbitals. Hall and Lennard-Jones [8] have discussed this in detail. The banana bonds show a fairly small contribution of the *s*- and 2$p\sigma$-type functions, the 2$p\pi$-contribution is dominating.

F_2 (Table 10)

Localization gives an inner shell orbital, three trigonally equivalent lone pair orbitals on each F atom and a bond orbital which is mostly formed by the 2$p\sigma$-functions (Table 10). No preferential orientation of the two sets of trigonal lone pair orbitals with respect to each other exist, which agrees with earlier studies [4, 9]. For a group-theoretical explanation see the recent article of England [18].

6. Conclusions

In this paper we have presented the applications of the density localization method to a number of homonuclear diatomic molecules. A good agreement between the ELMO's and DLMO's was found, as expected. For most of the atoms and molecules investigated so far the LMO's calculated by the four localization methods agree qualitatively and frequently quantitatively with the exception of the C_2 molecule, which seems to present a particular case. The best quantitative agreement is found in general between the ELMO's and the BLMO's. The agreement between the ELMO's and DLMO's is about as satisfactory, whereas the MPLMO's show sometimes a more marked difference.

All four methods have their justification and it depends on the problem under investigation (and on the preference of the user) which method is to be applied.

The Edmiston-Ruedenberg method is completely general and works reliably in all cases examined so far. It is the only method which uses the energy criterion for the localization. Unfortunately the computation time needed to determine the ELMO's is considerable. The density localization method stresses the charge density aspect of the electronic structure of atoms and molecules. This method is completely general as well, but appears to be more sensitive against the choice of the wavefunction at least in a few cases (C_2, N_2). From the physical point of view it is complementary to the energy localization method. Examining the calculations we can establish this method as a new localization method which adds information to our knowledge about the concept of localization and of localized orbitals. The procedures of Boys and of Magnasco and Perico have the advantage of requiring very little computation time. The method of Boys is intrinsic in character and simple in its structure. Therefore we tend to prefer it over the localization procedure of Magnasco and Perico. The restrictions to the applicability of this method seem to be of minor importance. As discussed before the Magnasco-Perico localization method is external in character, the MPLMO's thus depend on our choice of the orbital structure. This is in some respect a disadvantage limiting the applicability of the method, but for some purposes this may give an added flexibility which can be of use.

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References

1. von Niessen, W.: Density localization of atomic and molecular orbitals I. J. chem. Physics **55**, 4290 (1972).
2. Edmiston, C., Ruedenberg, K.: Rev. mod. Physics **35**, 457 (1963).
3. Ruedenberg, K.: Modern quantum chemistry, Vol. I. Sinanoğlu, O. (Ed.), p. 85. New York: Academic Press 1965.
4. Edmiston, C., Ruedenberg, K.: J. chem. Physics **43**, S 97 (1965).
5. Foster, J. M., Boys, S. F.: Rev. mod. Physics **32**, 300 (1960).
6. Boys, S. F.: Quantum theory of atoms, molecules, and the solid state. Löwdin, P. O. (Ed.), p. 253. New York: Academic Press 1966.
7. Magnasco, V., Perico, A.: J. chem. Physics **47**, 971 (1967); **48**, 800 (1968).
8. Lennard-Jones, J.: Proc. Roy. Soc. (London) A **198**, 1, 14 (1949). – Hall, G. G., Lennard-Jones, J.: Proc. Roy. Soc. (London) A **202**, 155 (1950). – Lennard-Jones, J., Pople, J. A.: Proc. Roy. Soc. (London) A **202**, 166 (1950). – Hall, G. G.: Proc. Roy. Soc. (London) A **202**, 336 (1950). – Pople, J. A.: Proc. Roy. Soc. (London) A **202**, 323 (1950). – Hall, G. G., Lennard-Jones, J.: Proc. Roy. Soc. (London) A **205**, 357 (1951).
9. Edmiston, C., Ruedenberg, K.: Quantum theory of atoms, molecules, and the solid state. Löwdin, P. O. (Ed.), p. 263. New York: Academic Press 1966.
10. Ransil, B. J.: Rev. mod. Physics **32**, 239 (1960).
11. Preuss, H.: Z. Naturforschg. **20** a, 1290 (1965).
12. Clementi, E.: J. chem. Physics **46**, 4737 (1967).
13. Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).
14. Whitten, J. L.: J. chem. Physics **44**, 359 (1966).
15. von Niessen, W.: Density localization of atomic and molecular orbitals III, to be submitted.
16. Trindle, C., Sinanoğlu, O.: J. chem. Physics **49**, 65 (1968).
17. The detailed results (basis set, expansion coefficients for the canonical MO's and LMO's and transformation matrices) can be obtained upon request from the author.
18. England, W.: Int. J. quant. Chemistry **5**, 683 (1971).

Dr. W. von Niessen
Max-Planck-Institut für Physik und Astrophysik
D-8000 München 23, Föhringer Ring 6
Germany