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# A fast intrinsic localization procedure applicable for *ab initio* and semiempirical linear combination of atomic orbital wave functions

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A new intrinsic localization algorithm is suggested based on a recently developed mathematical measure of localization. No external criteria are used to define *a priori* bonds, lone pairs, and core orbitals. It is shown that the method similarly to Edmiston–Ruedenberg’s localization prefers the well established chemical concept of  $\sigma$ – $\pi$  separation, while on the other hand, works as economically as Boys’ procedure. For the application of the new localization algorithm, no additional quantities are to be calculated, the knowledge of atomic overlap integrals is sufficient. This feature allows a unique formulation of the theory, adaptable for both *ab initio* and semiempirical methods, even in those cases where the exact form of the atomic basis functions is not defined (like in the EHT and PPP calculations). The implementation of the procedure in already existing program systems is particularly easy. For illustrative examples, we compare the Edmiston–Ruedenberg and Boys localized orbitals with those calculated by the method suggested here, within both the CNDO/2 and *ab initio* frameworks (using STO-3G and 6-31G\*\* basis sets) for several molecules (CO, H<sub>2</sub>CO, B<sub>2</sub>H<sub>6</sub>, and N<sub>2</sub>O<sub>4</sub>). Some similarities concerning the localization procedures of von Niessen as well as Magnasco and Perico are also discussed.

## I. INTRODUCTION

The introduction of localized molecular orbitals into the theoretical description of molecules has played an important role in understanding such classical chemical concepts as bonds, nonbonding electron pairs, core orbitals, and valency in terms of quantum mechanics. Foster and Boys<sup>1–3</sup> developed a criterion for calculating optimum localized orbitals, later Edmiston and Ruedenberg<sup>4–6</sup> as well as von Niessen<sup>7</sup> found different optimum localization functionals. The method of Edmiston and Ruedenberg became popular in early applications, since it preserves the separation of the energetically quite different  $\sigma$  and  $\pi$  orbitals of double bonds. On the other hand, Boys’ localization generates almost the same orbitals as the previous ones, except for double bonds where two equivalent  $\tau$  (banana) orbitals, proportional to the linear combinations  $\sigma + \pi$  and  $\sigma - \pi$ , result. In spite of the theoretical advantages of the Edmiston–Ruedenberg (ER) procedure, the computational complexity of each iterative step increases like  $N^5$  with the number of electrons  $N$ , while Boys’ algorithm behaves<sup>8</sup> like  $N^3$ . Because of this fact Boys’ localization is used almost exclusively in contemporary applications.<sup>9</sup> Although von Niessen’s method also gives excellent results, its algorithmic behavior is similar to that of the Edmiston–Ruedenberg procedure which restricts its practical application to smaller molecular systems. A fast alternative for solving the localization problem is the “external” localization of Magnasco and Perico,<sup>10</sup> but unfortunately, this method has the theoretical disadvantage that additional (not *ab initio*) requirements like *a priori* definitions of bonds, lone pairs, and core orbitals have to be intro-

duced.<sup>10–12</sup> This causes the resulting orbitals to be “prescribed,” displaying our expectations instead of the requirements of nature.

Localized orbitals are extensively used in the recent literature<sup>13,14</sup> especially for treating electron correlation problems of larger molecules by defining localized orbitals in the virtual MO subspace<sup>9,12,15</sup> and by using the diagrammatic version of the many-body perturbation theory based on localized orbitals.<sup>16–18</sup> Coupled cluster theory using localized orbitals has also been studied.<sup>19–21</sup> Applications of localized orbitals in multireference CI calculations and in studying molecular interactions can be found in Ref. 22. Expectations of neglecting the interaction between separated localized orbitals of large molecules were also studied<sup>23,24</sup> and developments on optimization algorithms<sup>8,25–30</sup> show a continuing interest in localization methods.

Localized orbitals are of importance in characterizing the shape of the three-dimensional “body” of molecular electron distributions, for example, in terms of the shapes of formal bonding and lone electron pairs. For this purpose the shape group method<sup>31–36</sup> (SGM), based on the homology groups of truncated contour surfaces is applicable. The shape variations of localized orbitals in a sequence of molecules may be correlated with chemical behavior. For example, the shapes of localized MOs representing lone electron pairs are of importance in protonation reactions.

One of our goals in developing efficient localization procedures is the analysis of the interrelations between reactivity and molecular shapes. These and similar problems can be studied by analyzing the shapes of localized orbitals, using the three-dimensional shape group and shape code techniques, based on a topological analysis.

The aim of this article is to study the capabilities of a

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new intrinsic localization algorithm. This method does not require any external criteria (unlike Magnasco-Perico localization) and, as will be shown, gives nearly identical results with the Edmiston-Ruedenberg process. On the other hand, its algorithmic behavior is  $N^3$  and no extra integrals (like dipole matrix elements) need be calculated.

In the first part of the paper the existing localization criteria are summarized in order to make the comparison with the proposed method easier. In the second part, the localization functional of the new procedure based on Mulliken atomic populations is described and the formulas of the optimization method are also elaborated. The stability of the optimum localized orbitals is studied in Sec. IV. Section V is devoted to the theoretical investigation of  $\sigma$ - $\pi$  separation and it will be shown that this is an inherent mathematical property of the localization functional proposed by us. A comparison with von Niessen's and Magnasco-Perico's approaches can be found in Sec. VI. In Sec. VII the behavior of the new procedure is studied by numerical and graphical comparisons of localized orbitals obtained by different methods. Since the new algorithm is equally applicable for *ab initio* and semiempirical wave functions, STO-3G, 6-31G\*\* and CNDO/2 results are also compared. The convergence properties of the various methods are also studied.

## II. INTRINSIC LOCALIZATION CRITERIA

Excellent review articles of localization procedures can be found in the literature (see, e.g., Refs. 8, 29, 37, and 38). Here we shall briefly summarize the various methods in order to unify notations. Single determinant Hartree-Fock wave functions composed of  $N$  molecular orbitals  $\{\varphi_i(\mathbf{r}), i = 1 \cdots N\}$  (we shall extensively use Dirac's notations  $|i\rangle$ ) are invariant to any unitary transformation  $U$  of the occupied orbitals

$$|i'\rangle = \sum_{j=1}^N U_{ji} |j\rangle \quad (1)$$

$$UU^\dagger = 1.$$

The aim of all localization procedures is to find a unitary transformed orbital set  $\{|i'\rangle\}$  which satisfies a given optimum localization criterion. Introducing the notation

$$\langle ij|\Omega|kl\rangle = \int \varphi_i^*(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\Omega(\mathbf{r}_1\mathbf{r}_2)\varphi_k^*(\mathbf{r}_1)\varphi_l(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2, \quad (2)$$

where  $\Omega$  is an appropriate two-electron operator, the three well known intrinsic localization methods can be summarized as follows:

Boys' procedure<sup>1-3</sup> minimizes the spatial extension of the MOs,

$$B\{\varphi_i\} = \sum_{i=1}^N \langle ii|\Omega^B|ii\rangle \quad (3a)$$

with

$$\Omega^B(\mathbf{r}_1, \mathbf{r}_2) = (\mathbf{r}_1 - \mathbf{r}_2)^2. \quad (3b)$$

This functional can be transformed into two equivalent forms. Simple algebraic manipulation leads to

$$B\{\varphi_i\} = -(2/N)B^1\{\varphi_i\} + 2\text{Tr}(r^2) - (2/N)[\text{Tr}(\mathbf{r})]^2 \quad (4)$$

or

$$B\{\varphi_i\} = -2B^2\{\varphi_i\} + 2\text{Tr}(r^2), \quad (5)$$

where

$$B^1\{\varphi_i\} = \sum_{i>j=1}^N [\langle i|\mathbf{r}|i\rangle - \langle j|\mathbf{r}|j\rangle]^2 \quad (6)$$

and

$$B^2\{\varphi_i\} = \sum_{i=1}^N [\langle i|\mathbf{r}|i\rangle]^2. \quad (7)$$

Since the traces of operators in Eqs. (4) and (5) are invariant to unitary transformations (1), the task of finding the minimum of  $B$  is equivalent to maximizing the distances between orbital centroids (function  $B^1$ ) or maximize the sum of squares of distances of orbital centroids from the origin of the coordinate system (functional  $B^2$ ).

The Edmiston-Ruedenberg method<sup>4-6</sup> seeks the maximum of the self-repulsion energy,

$$\text{ER}\{\varphi_i\} = \sum_{i=1}^N \langle ii|\Omega^{\text{ER}}|ii\rangle \quad (8a)$$

with

$$\Omega^{\text{ER}}(\mathbf{r}_1, \mathbf{r}_2) = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}. \quad (8b)$$

The localization introduced by von Niessen<sup>7</sup> maximizes the charge-density overlap functional,

$$N\{\varphi_i\} = \sum_{i=1}^N \langle ii|\Omega^N|ii\rangle \quad (9a)$$

with

$$\Omega^N(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (9b)$$

All of the above functionals are invariant with respect to rotations and translations of the molecular coordinate system except for  $B^2$ , which depends on the choice of the origin of the reference system.

The generally applied optimization algorithm originally suggested by Edmiston and Ruedenberg<sup>4,5</sup> determines the optimum unitary transformation of the form (1) by consecutive two by two rotations

$$|s'\rangle = \cos \gamma |s\rangle + \sin \gamma |t\rangle \quad (10a)$$

$$|t'\rangle = -\sin \gamma |s\rangle + \cos \gamma |t\rangle \quad (10b)$$

until convergence is reached. Since all of the functionals  $B$ ,  $B^1$ ,  $B^2$ , ER, and  $N$  depend on the MOs  $|i\rangle$  to the fourth power, the change due to the rotation (10) can be transformed to the common form

$$G\{\varphi_i'\} = G\{\varphi_i\} + A_{st} - A_{st} \cos 4\gamma + B_{st} \sin 4\gamma, \quad (11)$$

where  $G$  stands for any of the above functionals. If  $A_{st}^2 + B_{st}^2 \neq 0$ , then

$$G\{\varphi_i'\} = G\{\varphi_i\} + A_{st} + (A_{st}^2 + B_{st}^2)^{1/2} \cos 4(\gamma - \alpha). \quad (12)$$

The angle  $\alpha$  is defined by

$$\sin 4\alpha = B_{st}/(A_{st}^2 + B_{st}^2)^{1/2}, \quad (13a)$$

$$\cos 4\alpha = -A_{st}/(A_{st}^2 + B_{st}^2)^{1/2}, \quad (13b)$$

$$0 \leq \alpha < \pi/2. \quad (13c)$$

The definition of  $A_{st}$  and  $B_{st}$  differ from case to case. For the functionals  $B$ , ER, and  $N$

$$A_{st} = \langle st | \Omega | st \rangle - (1/4) [\langle ss | \Omega | ss \rangle + \langle tt | \Omega | tt \rangle - 2\langle ss | \Omega | tt \rangle], \quad (14a)$$

$$B_{st} = \langle ss | \Omega | st \rangle - \langle tt | \Omega | st \rangle \quad (14b)$$

with the appropriate operators  $\Omega^B$ ,  $\Omega^{ER}$  and  $\Omega^N$ , respectively. Application of the above formulas requires the calculation of the two-electron MO integrals (2) from the atomic integral set, that causes the Edmiston–Ruedenberg and von Niessen's methods behave computationally<sup>8</sup> like  $N^5$ . A much more economical way to perform Boys' localization is to maximize functional  $B^2$ . In this case

$$A_{st} = \langle s | r | t \rangle^2 - (1/4) [\langle s | r | s \rangle - \langle t | r | t \rangle]^2, \quad (15a)$$

$$B_{st} = \langle s | r | t \rangle [\langle s | r | s \rangle - \langle t | r | t \rangle]. \quad (15b)$$

Determination of the quantities  $A_{st}$  and  $B_{st}$  requires only the calculation of the one-electron dipole integrals  $\langle s | r | s \rangle$ ,  $\langle t | r | t \rangle$  and  $\langle s | r | t \rangle$ , that makes the algorithmic behavior of Boys' method<sup>8</sup>  $N^3$ . This property favors the computational application of Boys localization against the ER or  $N$  method.

Maximization of expression (12) leads to a choice for the rotation angle

$$\gamma = \alpha + k\pi/2 \quad (16)$$

while for minimization the values

$$\gamma = \alpha + (2k + 1)\pi/4 \quad (17)$$

have to be selected with an arbitrary integer  $k$ . This ambiguity of the determination of the rotation angle was analyzed by Barr and Basch<sup>25</sup> and we will also discuss the problem later from a different point of view.

### III. LOCALIZATION OF THE MULLIKEN ATOMIC CHARGE DISTRIBUTION

We have shown in a recent article<sup>39</sup> that for LCAO molecular orbitals  $|i\rangle$  a localization quantity  $d_i$  can be defined that measures the number of atoms over which the MO extends. The measure of localization is defined by the expression

$$d_i = \left\{ \sum_{A=1}^n (Q_A^i)^2 \right\}^{-1}, \quad (18)$$

where  $A$  stands for the various atoms of the molecule,  $n$  is the number of atoms, and  $Q_A^i$  are the gross atomic Mulliken populations of the orbital  $|i\rangle$ . Quantity  $d_i$ , generally non-integer, has the property

$$0 < d_i \leq n \quad (19)$$

and it gives, to an excellent approximation, the number of atoms where the orbital is localized.

A mean delocalization  $D$  of the constituent MOs of the one-determinant wave function can also be defined as

$$D^{-1} = N^{-1} \sum_{i=1}^N d_i^{-1}. \quad (20)$$

It has been shown that for one-determinant wave functions,  $D$  is a bounded quantity

$$0 < D \leq D_{\max} \leq n, \quad (21)$$

where

$$D_{\max} = N^2 / \sum_{A=1}^n Q_A^2 = \left( \sum_{A=1}^n Q_A \right)^2 / \sum_{A=1}^n Q_A^2. \quad (22)$$

Here  $Q_A$  stands for the total atomic charges (populations) which are invariant to any unitary transformation (1).

Since  $D$  measures the mean extension of the one-electron orbitals, the basic idea of the procedure which we shall call later on "population localization" is to find a unitary transformation (1) which minimizes  $D$ . This task can be accomplished in an analogous way to the previously discussed intrinsic localization methods by using the operator expectation value definition<sup>40,41</sup> of Mulliken's gross orbital populations.

For each atomic basis function  $|\mu\rangle$  let us introduce the Hermitian operator

$$P_\mu = P_\mu^\dagger = (1/2) \{ |\tilde{\mu}\rangle \langle \mu| + |\mu\rangle \langle \tilde{\mu}| \}, \quad (23)$$

where

$$|\tilde{\mu}\rangle = \sum_{\nu} (\mathbf{S}^{-1})_{\nu\mu} |\nu\rangle \quad (24)$$

and  $\mathbf{S}$  means the atomic overlap matrix

$$S_{\mu\nu} = \langle \mu | \nu \rangle. \quad (25)$$

The functions  $\{|\tilde{\mu}\rangle\}$  form the biorthogonal vector system of the atomic basis set  $\{|\mu\rangle\}$ . It is a usually accepted assumption that an "atom"  $A$  in a molecule can be represented by the set of its atomic orbitals. The atomic population operators are defined by

$$P_A = P_A^\dagger = \sum_{\mu \in A} P_\mu, \quad (26)$$

where the summation runs over the AOs which belong to the atom  $A$ . The gross atomic population of a normalized molecular orbital  $|i\rangle$  can be written as

$$Q_A^i = \langle i | P_A | i \rangle. \quad (27)$$

One can easily verify that this definition leads (except for a spin factor of 2) to the same expressions originally introduced by Mulliken.<sup>42,43</sup>

For the maximum of  $D^{-1}$  one obtains the optimum functional  $\mathcal{P}$  of the population localization by dropping the factor  $N^{-1}$  from (20) and substituting Eqs. (18) and (27)

$$\mathcal{P}\{\varphi_i\} = \sum_{i=1}^N \sum_{A=1}^n [\langle i | P_A | i \rangle]^2. \quad (28)$$

Since both summations of the optimum functional run unrestricted over the MOs as well as over all of the atoms of the molecule, the optimization process generated by the maximization of  $\mathcal{P}$  does not apply any external criteria. Although a hidden subdivision of the molecule to atoms has been involved by defining the atomic population operators  $P_A$ , this step is generally accepted and contains no *a priori* information about the chemical structure of the molecule at all, so the population localization can be considered "essentially intrinsic."

Looking for the  $N \times N$  unitary matrix  $U$  again in the

form of consecutive two by two rotations (10), the change in the functional  $\mathcal{P}$  can be transformed to the general expressions (11) or (12), where

$$A_{st} = \sum_{A=1}^n \{ \langle s|P_A|t \rangle^2 - (1/4) [\langle s|P_A|s \rangle - \langle t|P_A|t \rangle]^2 \} \quad (29a)$$

$$B_{st} = \sum_{A=1}^n \langle s|P_A|t \rangle [\langle s|P_A|s \rangle - \langle t|P_A|t \rangle]. \quad (29b)$$

It is easy to recognize the analogy between the localization functionals  $B^2$  and  $\mathcal{P}$  as well as the corresponding expressions (15) and (29). As the calculation of the quantities  $A_{st}$  and  $B_{st}$  requires only the evaluation of the matrix elements of the one-electron operators  $P_A$ , the computational effort increases with the number of electrons like  $N^3$ , similarly to the Boys localization procedure.

For LCAO molecular orbitals the explicit form of a general matrix element of the operator  $P_A$  can be easily obtained by making use of the relation

$$\langle \rho|\tilde{\mu} \rangle = \delta_{\rho\mu} \quad (30)$$

which results in

$$\langle s|P_A|t \rangle = (1/2) \sum_{\rho} \sum_{\mu \in A} \{ c_{\rho}^{s*} S_{\rho\mu} c_{\mu}^t + c_{\mu}^{s*} S_{\mu\rho} c_{\rho}^t \}. \quad (31)$$

The first summation in Eq. (31) runs over all of the atomic basis functions, while the second summation contains only those AOs which belong to atom A. The expansion coefficients of the orbitals  $|s\rangle$  and  $|t\rangle$  are denoted by  $c_{\mu}^s$  and  $c_{\mu}^t$ , respectively. As we can see, for performing the iterative steps of the population localization, no calculation of extra integrals (like the dipole integrals for the Boys procedure) is necessary. The overlap integrals  $S_{\rho\mu}$ , on the other hand, are always accessible in all *ab initio* or semiempirical calculations, that makes the population localization method applicable even in those cases where the exact form of the atomic basis functions is not defined, as in EHT or PPP calculations.

#### IV. ORBITAL-STABILITY CONDITIONS

The unitary matrix  $U$  leading to optimum localized orbitals is usually constructed according to the original proposal of Edmiston and Ruedenberg.<sup>4,5</sup> The  $2 \times 2$  unitary transformations of the form (10) are performed on the  $N(N-1)/2$  orbital pairs until a predetermined convergence criterion is satisfied. As is well known, any arbitrary permutation of the MOs or change in sign does not affect the physical meaning of the  $N$ -electron one-determinant wave function. As a consequence of this fact it would be unphysical requiring that for a stable localized MO set the rotation (10) be the identity transformation for all orbital pairs  $(|s\rangle, |t\rangle)$ . Instead, even when a proper convergence has been achieved, the interchange of  $|s\rangle$  and  $|t\rangle$  or a change in sign are to be allowed. This convergence criterion which we will call later on "orbital-stability" condition is satisfied when  $\cos \gamma = \pm 1$  or  $\sin \gamma = \pm 1$  in transformation (10). These cases can be summarized as

$$\gamma = m\pi/2, \quad (32)$$

where  $m$  is an arbitrary integer number. For the functionals to be maximized,  $\gamma$  is chosen according to Eq. (16)

$$\gamma = \alpha + k\pi/2 = m\pi/2 \quad (33)$$

or

$$\alpha = (m - k)\pi/2. \quad (34)$$

Comparing Eq. (34) with restriction (13c), one obtains

$$\alpha = 0 \quad (35)$$

and

$$\sin 4\alpha = 0 \quad (36a)$$

$$\cos 4\alpha = 1. \quad (36b)$$

Considering expressions (13a) and (13b), the orbital-stability condition for a given MO pair  $(|s\rangle, |t\rangle)$  can be summarized as

$$B_{st} = 0 \quad (37a)$$

$$A_{st} < 0. \quad (37b)$$

For those functionals where the minimum is to be found, a similar derivation using Eq. (17) for  $\gamma$  shows that the orbital-stability criterion is

$$\alpha = \pi/4 \quad (38)$$

or

$$B_{st} = 0 \quad (39a)$$

$$A_{st} > 0. \quad (39b)$$

The orbital-stability concept leads to a solution of the problem of ambiguity in the determination of the rotation angle  $\gamma$  using Eqs. (16) or (17). Barr and Basch<sup>25</sup> have suggested that two possible rotations  $\gamma = \alpha$  and  $\gamma = \pi/2 - \alpha$  should be tested at each iteration step. Haddon and Williams<sup>26</sup> have found, on the other hand, that this treatment never improves the speed of convergence. The same is valid for the other proposal<sup>25,26</sup>: if transformation (10) with  $|\sin \gamma| > 0.9$  causes an orbital switching, then the resulting orbitals  $|s'\rangle$  and  $|t'\rangle$  are to be interchanged. Considering these facts, we suggest a definite choice for  $\gamma$  which automatically avoids orbital switching in the neighborhood of stable solutions. In the case of orbital-stable solutions the transformation matrix of Eq. (10) becomes identity if for maximization

$$\gamma = \alpha \quad (40)$$

and for minimization

$$\gamma = \alpha - \pi/4 \quad (41)$$

is chosen. These values coincide with those in the original proposal of Edmiston and Ruedenberg.<sup>4</sup>

The orbital-stability criteria (37) and (39) imply some additional relationships between integrals of the optimum localized orbitals. For the ER and von Niessen's method (37a) is equivalent to the well known relation<sup>4,7</sup>

$$\langle ss|\Omega|st \rangle = \langle tt|\Omega|st \rangle, \quad (42a)$$

while Eq. (37b) leads to a relation between the Coulomb and exchange interactions as well as self-Coulomb interactions of orbitals  $|s\rangle$  and  $|t\rangle$

$$2\langle st|\Omega|st \rangle + \langle ss|\Omega|tt \rangle < (1/2) [\langle ss|\Omega|ss \rangle + \langle tt|\Omega|tt \rangle]. \quad (42b)$$

For Boys localized orbitals the following expressions hold

$$\langle s|\mathbf{r}|t\rangle[\langle s|\mathbf{r}|s\rangle - \langle t|\mathbf{r}|t\rangle] = 0 \quad (43a)$$

$$\langle s|\mathbf{r}|t\rangle^2 - (1/4)[\langle s|\mathbf{r}|s\rangle - \langle t|\mathbf{r}|t\rangle]^2 < 0 \quad (43b)$$

for all pairs of MOs  $|s\rangle$  and  $|t\rangle$ . This set of relations could be satisfied if all off-diagonal matrix elements  $\langle s|\mathbf{r}|t\rangle$  were zero, or in other words, if the Boys localized orbitals were all eigenfunctions of the vector operator  $\mathbf{r}$ . Unfortunately, the components  $x, y, z$  of  $\mathbf{r}$  in the finite  $N$ -dimensional matrix representation of the occupied subspace do not commute any more, consequently, the eigenvalue problem of  $\mathbf{r}$  cannot be solved. On the other hand, the Boys localized orbitals can be considered as "generalized eigenfunctions" of the position operator  $\mathbf{r}$  in a finite  $N$ -dimensional subspace, in the sense that according to the equation

$$B^2\{\varphi_i\} = \text{Tr}(\mathbf{r}\mathbf{r}) - \sum_{i \neq j=1}^N |\langle i|\mathbf{r}|j\rangle|^2, \quad (44)$$

the Boys localized orbitals minimize the sum of amplitude squares of the off-diagonal matrix elements of  $\mathbf{r}$ . This interpretation is also supported by the analogy that in the infinite dimensional Hilbert space (where the eigenvalue problem can be solved) the eigenvectors of  $\mathbf{r}$  are completely localized  $\delta$  functions.

Formulas of the population localization method (28), (29a), and (29b) can be transformed exactly to that of the Boys procedure by introducing the atomic population vector operator  $\mathbf{P} = (P_1, P_2, \dots, P_n)$  and replacing  $\mathbf{r}$  by  $\mathbf{P}$ . According to the above arguments, the population localized orbitals are the generalized eigenfunctions of the population vector operator  $\mathbf{P}$  in the  $N$ -dimensional subspace of the occupied orbitals.

## V. $\sigma$ - $\pi$ SEPARATION

We will investigate in this section the orbital stability of (real)  $\sigma$  and  $\pi$  as well as  $\tau$  localized orbitals of planar molecules both for Boys and population localization methods. Orbital  $|\sigma\rangle$  is invariant to the reflection of the plane of the molecule while  $|\pi\rangle$  changes sign for this operation. The orbitals

$$|\tau\rangle = 2^{-1/2}(|\sigma\rangle + |\pi\rangle) \quad (45a)$$

$$|\tau'\rangle = 2^{-1/2}(|\sigma\rangle - |\pi\rangle) \quad (45b)$$

transform to each other for reflections. The position vector  $\mathbf{r} = \mathbf{r}_{\parallel} + \mathbf{r}_{\perp}$  can be partitioned to the orthogonal vectors  $\mathbf{r}_{\parallel}$  and  $\mathbf{r}_{\perp}$ , where  $\mathbf{r}_{\parallel}$  is parallel to the plane of the molecule and  $\mathbf{r}_{\perp}$  is normal to it. From symmetry considerations

$$\langle \sigma|\mathbf{r}|\sigma\rangle = \langle \sigma|\mathbf{r}_{\parallel}|\sigma\rangle = \mathbf{R}_{\sigma}, \quad (46a)$$

$$\langle \pi|\mathbf{r}|\pi\rangle = \langle \pi|\mathbf{r}_{\parallel}|\pi\rangle = \mathbf{R}_{\pi}, \quad (46b)$$

$$\langle \sigma|\mathbf{r}|\pi\rangle = \langle \pi|\mathbf{r}|\sigma\rangle = \langle \pi|\mathbf{r}_{\perp}|\sigma\rangle = \mathbf{S}. \quad (46c)$$

Using the definitions (45) and (46)

$$\langle \tau|\mathbf{r}|\tau\rangle = (\mathbf{R}_{\sigma} + \mathbf{R}_{\pi})/2 + \mathbf{S} \quad (47a)$$

$$\langle \tau'|\mathbf{r}|\tau'\rangle = (\mathbf{R}_{\sigma} + \mathbf{R}_{\pi})/2 - \mathbf{S} \quad (47b)$$

$$\langle \tau|\mathbf{r}|\tau'\rangle = \langle \tau'|\mathbf{r}|\tau\rangle = (\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})/2. \quad (47c)$$

Substituting the above expressions to Eqs. (15a) and (15b)

and considering the orthogonality of  $(\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})$  and  $\mathbf{S}$ , we obtain

$$B_{\sigma\pi} = (\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})\mathbf{S} = 0 \quad (48a)$$

$$A_{\sigma\pi} = \mathbf{S}^2 - (\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})^2/4 \quad (48b)$$

and

$$B_{\tau\tau'} = (\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})\mathbf{S} = 0 \quad (49a)$$

$$A_{\tau\tau'} = (\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})^2/4 - \mathbf{S}^2. \quad (49b)$$

From the orbital-stability criterion  $B_{st} = 0$ ,  $A_{st} < 0$  it follows that if the orbitals  $|\sigma\rangle$  and  $|\pi\rangle$  are well separated, i.e., if the following relation between the distance of their centroids and the  $\tau$ -centroid separation  $2\mathbf{S}$ ,

$$(\mathbf{R}_{\sigma} - \mathbf{R}_{\pi})^2 > (2\mathbf{S})^2 \quad (50)$$

holds, then the  $(|\sigma\rangle, |\pi\rangle)$  orbital pairs are preserved. In the more important case, however, when both the  $|\sigma\rangle$  and  $|\pi\rangle$  orbitals belong to the same bond, then  $\mathbf{R}_{\sigma} - \mathbf{R}_{\pi} \approx 0$ , and according to Eq. (49b) the  $\tau$ - $\tau'$  separation becomes stable instead.

For population localization let us consider the following facts. Since the orbitals  $|\tau\rangle$  and  $|\tau'\rangle$  are equivalent, their atomic populations have to be the same on all atoms of a planar molecule,

$$\langle \tau|P_A|\tau\rangle = \langle \tau'|P_A|\tau'\rangle. \quad (51)$$

It is easy to show using Eq. (45) that this equation holds only when

$$\langle \sigma|P_A|\sigma\rangle = Q_A^{\sigma} \quad (52a)$$

$$\langle \pi|P_A|\pi\rangle = Q_A^{\pi} \quad (52b)$$

$$\langle \sigma|P_A|\pi\rangle = \langle \pi|P_A|\sigma\rangle = 0 \quad (52c)$$

and

$$\langle \tau|P_A|\tau\rangle = \langle \tau'|P_A|\tau'\rangle = (Q_A^{\sigma} + Q_A^{\pi})/2 \quad (53a)$$

$$\langle \tau|P_A|\tau'\rangle = \langle \tau'|P_A|\tau\rangle = (Q_A^{\sigma} - Q_A^{\pi})/2. \quad (53b)$$

Substituting these expressions into Eq. (29), one finds that

$$B_{\sigma\pi} = 0 \quad (54a)$$

$$A_{\sigma\pi} = -(1/4) \sum_{A=1}^n (Q_A^{\sigma} - Q_A^{\pi})^2 < 0 \quad (54b)$$

and

$$B_{\tau\tau'} = 0 \quad (55a)$$

$$A_{\tau\tau'} = (1/4) \sum_{A=1}^n (Q_A^{\sigma} - Q_A^{\pi})^2 > 0. \quad (55b)$$

This result shows that for optimum population localized orbitals the  $\sigma$ - $\pi$  separation is always the stable solution.

We have shown earlier<sup>44</sup> that the maximum delocalized orbitals obtained by minimizing the optimum functional  $\mathcal{P}$  can possibly describe the reaction channels of interacting molecular systems. The crucial point of this interpretation has been the symmetry breaking behavior of the optimum delocalized orbitals. It is also possible to prove theoretically, using an argument similar to that given above, that the spontaneous symmetry breaking is a necessary consequence of the orbital-stability criterion (39) which is to be applied for orbitals minimizing (28).

## VI. COMPARISON WITH THE MAGNASCO-PERICO AND VON NIESSEN'S METHOD: THEORY

Although Magnasco and Perico<sup>10</sup> used the local orbital populations

$$P_i = \sum_{\rho \in \Gamma_i} \sum_{\mu \in \Gamma'_i} c_\rho^* S_{\rho\mu} c_\mu^i \quad (56)$$

with appropriately (externally) chosen  $\Gamma_i$  and  $\Gamma'_i$  sets of AOs for defining the localization functional

$$\text{MP}\{\varphi_i\} = \sum_{i=1}^N P_i, \quad (57)$$

our approach considerably differs from that in two respects. First, we do not apply the arbitrary sets  $\Gamma_i$  which differ for bonds, inner shells, lone pairs, etc., except for the partitioning to atoms. In the case of atomic partitioning,  $\Gamma_i = \Gamma'_i = A$  but  $P_i \neq \langle t | P_A | t \rangle$ , since comparing Eq. (56) to Eq. (31)  $P_i$  gives the net atomic population on atom A while  $\langle t | P_A | t \rangle$  is the gross Mulliken population on the same atom. The second difference can be found in the structure of the optimum functionals. The localization functional MP is linear in  $P_i$ , by contrast, the population localization optimizes functional (28) which is of second order of the atomic populations  $Q_A^i$ . This emphasizes large  $Q_A^i$  values and diminishes smaller ones making in this way the avoidance of preselected bonding regions  $\Gamma_i$  possible.

The method of von Niessen maximizes the self charge overlap (9a) of the MOs. Our procedure is conceptually similar but the charge overlap is "discretized" to atoms first according to Eqs. (18) and (28). This suggests that similar results can be expected from both localizations, nevertheless, the methods cannot be transformed even approximately into each other. Perkins and Stewart<sup>45</sup> have proposed a ZDO version of von Niessen's procedure with the localization functional

$$\text{PS}\{\varphi_i\} = \sum_{i=1}^N \sum_{A=1}^n \left\{ \sum_{\mu \in A} (c_\mu^i)^2 \right\}^2. \quad (58)$$

A consistent application of the ZDO approximation to Eq. (9a) shows, however, that

$$N^{\text{ZDO}}\{\varphi_i\} = \sum_{i=1}^N \sum_{A=1}^n \left\{ \sum_{\mu \in A} (c_\mu^i)^4 \langle \mu\mu | \Omega^N | \mu\mu \rangle \right\}. \quad (59)$$

The weight factors  $\langle \mu\mu | \Omega^N | \mu\mu \rangle$  strongly depend on the orbital exponents of the normalized atomic orbitals  $|\mu\rangle$  and cannot be treated as common factors in the functional (59). Instead, what the above authors have really found is the ZDO approximation to the population localization functional  $\mathcal{P}$  presently proposed by us.

## VII. COMPARISON WITH BOY'S AND EDMISTON-RUEDENBERG'S LOCALIZATION: NUMERICAL RESULTS

The aim of these numerical calculations is to study the capabilities of the population localization method for both semiempirical (CNDO/2) and *ab initio* wave functions.

The purpose of the actual choices of model molecules for the calculations is to test the method in different physical situations. In carbon monoxide, a triple bond and the pecu-

liar single lone pair of carbon can be studied, while formaldehyde serves as a test case for single and double bonds as well as for the double lone pairs of oxygen. The new procedure is tested for describing partial BHB bonds in the case of diborane. Another special physical situation of the five valued nitrogen containing  $\text{N}_2\text{O}_4$  molecule is also investigated.

We have chosen STO-3G as the first Gaussian basis set since this is the closest to the CNDO/2 Slater basis extended by inner shell AOs. It can be expected that polarization functions can play an important role on the bridge hydrogen atoms of  $\text{B}_2\text{H}_6$  and on the five valued nitrogens of  $\text{N}_2\text{O}_4$ . Therefore the 6-31G\*\* basis has also been used where applicable, and the basis 6-31G\* for the molecules containing heavy atoms only.

Population and ER localizations were carried out for CNDO wave functions while *ab initio* occupied MOs were localized by the population and Boys methods. The population and ER localization programs were written by us, the Boys localized orbitals were determined by the MONSTER-GAUSS package.

The Cartesian coordinates of the atoms of the molecules calculated can be found in Table I.

The first question studied has been the ability of the proposed localization method for separating orbitals located on the same atom with multiple basis functions. The answer is not quite clear from the form (28) of the localization function  $\mathcal{P}$  itself but the considerations used at the orbital-stability studies can be applied here, too. The overlap between AOs of the same atom are zero and with AOs on distant

TABLE I. Descartes coordinates of the atoms in a.u. for the molecules studied.

Molecule Atom	X	Y	Z
<b>CO<sup>a</sup></b>			
O	0.0	0.0	2.132
C	0.0	0.0	0.0
<b>H<sub>2</sub>CO<sup>b</sup></b>			
O	0.0	0.0	2.282 5
C	0.0	0.0	0.0
H1	1.793 388	0.0	-1.109 7
H2	-1.793 388	0.0	-1.109 7
<b>B<sub>2</sub>H<sub>6</sub><sup>c</sup></b>			
H1	-1.947 40	0.0	-2.824 25
H2	-1.947 40	0.0	2.824 25
H3	1.947 40	0.0	-2.824 25
H4	1.947 40	0.0	2.824 25
H5	0.0	-1.894 71	0.0
H6	0.0	1.894 71	0.0
B1	0.0	0.0	-1.677 15
B2	0.0	0.0	1.677 15
<b>N<sub>2</sub>O<sub>4</sub><sup>a</sup></b>			
N1	0.0	-1.653 532	0.0
N2	0.0	1.653 532	0.0
O1	-2.050 381	-2.530 377	0.0
O2	2.050 381	-2.530 377	0.0
O3	-2.050 381	2.530 377	0.0
O4	2.050 381	2.530 377	0.0

<sup>a</sup> From Ref. 27.

<sup>b</sup> From Ref. 28.

<sup>c</sup> From Ref. 46.

TABLE II. Core-valence separations. Coefficients of the 1s basis functions in the LCAO expansion of the core MOs.

Molecule	Atom	STO-3G MOs			6-31G** MOs		
		Canonical	Boys localized	Population localized	Canonical	Boys localized	Population localized
CO	O	0.9941	1.0107	1.0250	0.9947	1.0094	1.0187
	C	0.9936	1.0106	1.0189	0.9960	1.0093	1.0161
H <sub>2</sub> CO	O	0.9943	1.0132	1.0251	0.9947	1.0101	1.0168
	C	0.9926	1.0036	1.0036	0.9957	1.0055	1.0070
B <sub>2</sub> H <sub>6</sub>	B	0.9901	1.0004	1.0005	0.9962	1.0043	1.0072
N <sub>2</sub> O <sub>4</sub>	N	0.9939	1.0053	1.0250	0.9948	1.0056	1.0047
	O	0.9944	1.0141	1.0027	0.9952	1.0107	1.0147

atoms are small, hence Eq. (31) implies that the off-diagonal matrix elements  $\langle s|P_A|t \rangle$  are negligible. Consequently, expressions (29) and (37) show the stability of the above kind of orbitals during the iteration process. As an illustration, we collected the core-AO LCAO coefficients of the inner shell orbitals calculated by various methods in Table II. As it can be seen, the valence-core separation becomes even more emphasized when compared to the canonical MOs, both for Boys and population localized MOs of all of the molecules studied. The core LCAO coefficients of the population localized orbitals are greater than one and close to those of the Boys MOs, although usually somewhat greater.

The valence localized orbitals calculated by various methods are shown and compared in Figs. 1 to 7. The positive and negative parts of the wave functions are distinguished by solid and dashed lines starting at the absolute values of 0.1 a.u., followed by consecutive contour lines at  $\pm 0.1$  increments. The left-hand sides of the figures show the population localized orbitals while the corresponding ER orbitals (for CNDO) and Boys localized orbitals (for *ab initio* calculations) are shown for comparison on the right-hand side.

The carbon and oxygen lone pairs of carbon monoxide are shown in Fig. 1. In the CNDO approximation, the requirement of  $\sigma$ - $\pi$  separation determines uniquely the localized MOs, therefore the results of population and ER localizations are identical. For *ab initio* calculations the Boys lone pairs exhibit considerable delocalization tails along the C-O bond, however the corresponding population localized orbitals are well localized, indeed, on the given atom.

The bonding orbitals of CO are shown in Fig. 2. As follows from symmetry, the ER orbitals are again equivalent to the population localized ones. The population localization leads to one  $\sigma$  and two equivalent orthogonal  $\pi$  orbitals in all approximations. On the other hand, Boys localization gives three equivalent  $\tau$  orbitals which can be transformed to one another by rotations of 120 deg around the C-O bond. The improvement in the quality of basis set makes the LOs slightly more compact and the addition of polarization functions results in more detailed structures around the nuclei.

The two lone pairs of formaldehyde are plotted in Fig. 3. The population localization and ER results are practically the same (a very small numerical difference can be found in Table III). The population method prefers  $\sigma$ - $\pi$ -like symmetry separation for lone pairs, too, where one of the lone pairs correspond to the  $p_x$  AO of the oxygen. Boys localization results in two symmetrical  $\tau$ -like lone pairs which transform to each other by reflection. These orbitals have also a delocalization tail towards the carbon atom.

The  $\sigma$ - $\pi$  as well as  $\tau$  separation for the double bond of H<sub>2</sub>CO are illustrated in Fig. 4. Qualitatively the same conse-

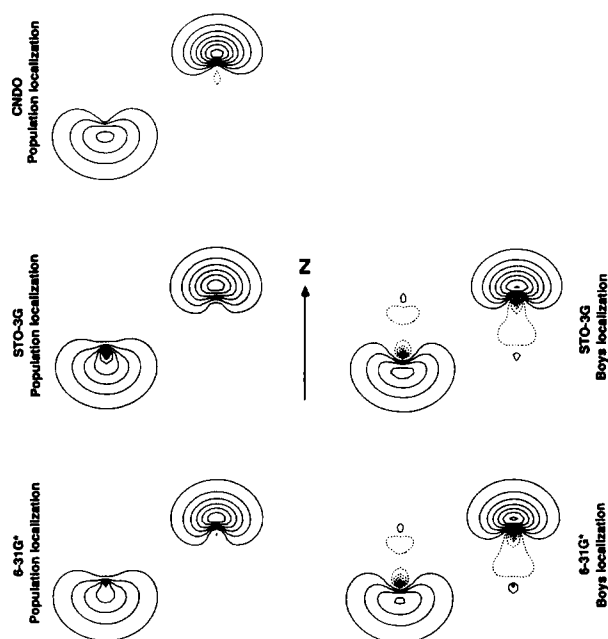


FIG. 1. Contour plots of the localized carbon and oxygen lone-pair orbitals of carbon monoxide. The positions of the atoms are specified in Table I. Positive contour values are indicated by solid lines, the dashed curves mean negative wave function values. The first contours lines start at the absolute values of 0.1 a.u., followed by others at  $\pm 0.1$  a.u. increments. The Edmiston-Ruedenberg orbitals are not shown here, since they are equivalent to the population localized MOs in the CNDO/2 approximation.



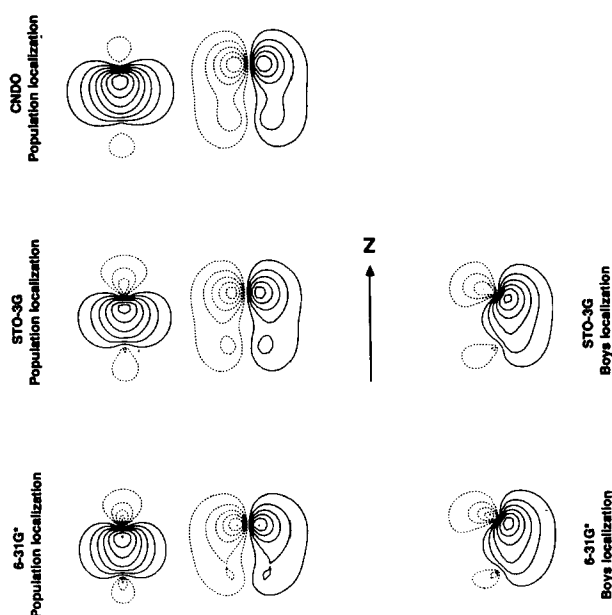


FIG. 2. The bonding orbitals of the CO molecule calculated by various localization methods. Population localized  $\sigma$  and  $\pi$  orbitals are shown on the left-hand side of the figure, the Boys localized  $\tau$  orbitals can be found on the right-hand side. The ER orbitals are equivalent to the population localized ones. The contour values are the same as in Fig. 1.

quences hold for this case what we have found for carbon monoxide, except for the fact that only one  $\pi$  and two symmetrical  $\tau$  orbitals are obtained for the C–O bond. Again, the ER and population localized orbitals are in close agreement.

The C–H bond of formaldehyde behaves very similarly to the B–H bond of diborane, which is shown in Fig. 5 together with the B–H–B bridge bond. As we can see, the re-

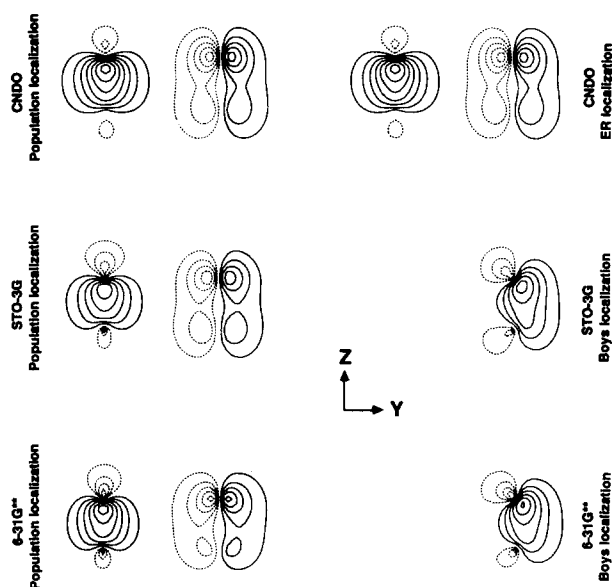


FIG. 4. The population- and ER-localized  $\sigma$  and  $\pi$  and Boys localized  $\tau$  bonding orbitals of formaldehyde. The positions of the atoms are specified in Table I. The contour values are the same as in Fig. 1.

sulting orbitals are almost independent of the applied localization method in a given approximation. It is to be observed that the common expectations that polarization functions can play a considerable role in the shape of localized orbitals are not justified.

The population localized lone-pair orbitals of  $N_2O_4$  show an approximate  $\sigma$ – $\pi$ -like separation in Fig. 6. This is quite a remarkable feature considering the fact that the sur-

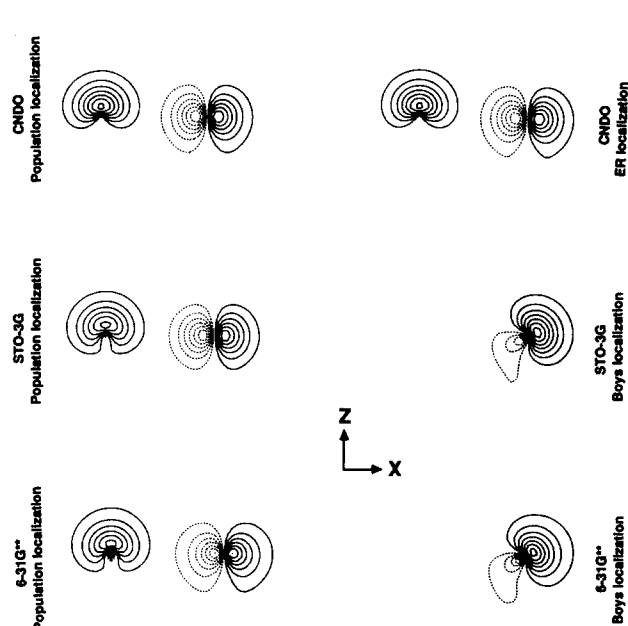


FIG. 3. Oxygen lone pairs of the formaldehyde calculated by various methods. The contour lines indicate the same values as in Fig. 1.

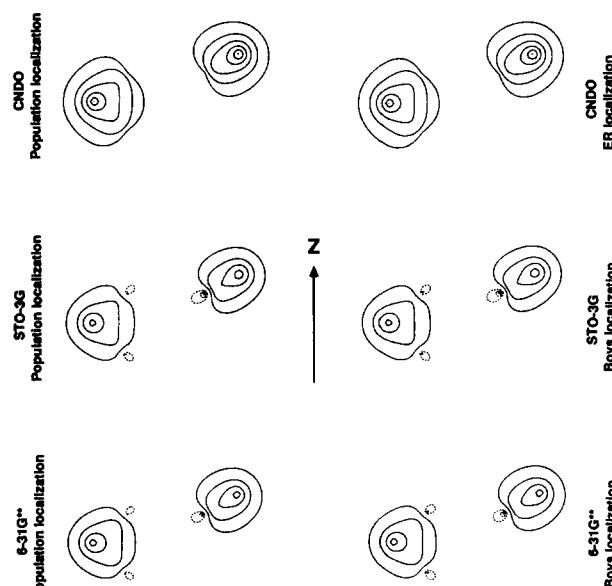


FIG. 5. The BHB bridge bond and BH terminal bond of  $B_2H_6$  in various approximations. The BHB bond (first from left) lies in the  $yz$  plane, while the BH bond (second from left) in the  $xz$  plane. The contour lines indicate the same values as in Fig. 1.

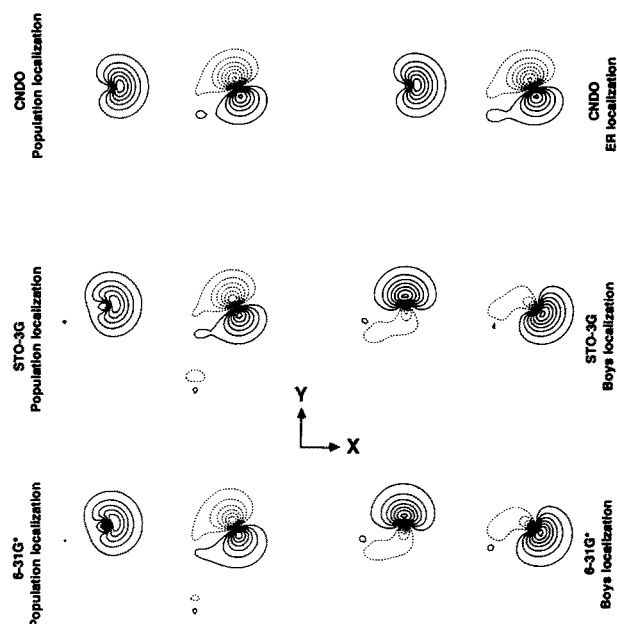


FIG. 6. The oxygen lone-pair orbitals of the  $O_4$  atom (see Table I.) in the  $xy$  plane of the  $N_2O_4$  molecule. The contour lines indicate the same values as in Fig. 1.

roundings of the N–O bonds do not reflect the corresponding symmetry. The orbital similar to the  $p_x$ -like lone pair of the formaldehyde oxygen is strongly polarized towards the nitrogen, describing in this way a partial  $\pi$  bond (lying in the plane of the molecule!) between the nitrogen and oxygen atoms. Again, the Boys localization prefers two (almost) symmetrical  $\tau$ -like lone pairs which are strongly polarized along the N–O bond.

The contour plots of the N–N bond can be found in Fig. 7. All localization procedures give LOs of similar shapes, except for the large delocalization tails of the Boys orbitals on the surrounding oxygens. As a rule for this molecule, the addition of  $d$  functions to the atomic basis set increases the localization to a great extent, that underlines the particular importance of polarization functions for nitrogens of formally five valences. The  $\sigma$  and  $\pi$  orbitals of the N–O double bonds show qualitatively the same properties as the corresponding orbitals of the C–O bond in formaldehyde.

In Table III, we summarized the values of the localization functionals for various approximations, molecules and localization methods. For the sake of comparisons we have used the translational invariant Boys functional  $B^1$ . As we can see the functional values of ER and population localized orbitals are always in good agreement while for Boys localized orbitals this holds only for  $B_2H_6$  where  $\sigma$ – $\pi$  separation does not appear.

On intuitive basis one could expect that symmetry-based  $\sigma$ – $\pi$  separation and the possibilities of extensive  $\pi$  systems enhance the success of the proposed delocalization method. Note, however, that symmetry-based  $\sigma$ – $\pi$  separation is not a prerequisite. The delocalization method is applicable to  $\sigma$  frameworks, as it has been shown for the proton +  $H_2O$  scattering process.<sup>44</sup> Furthermore, maximum delo-

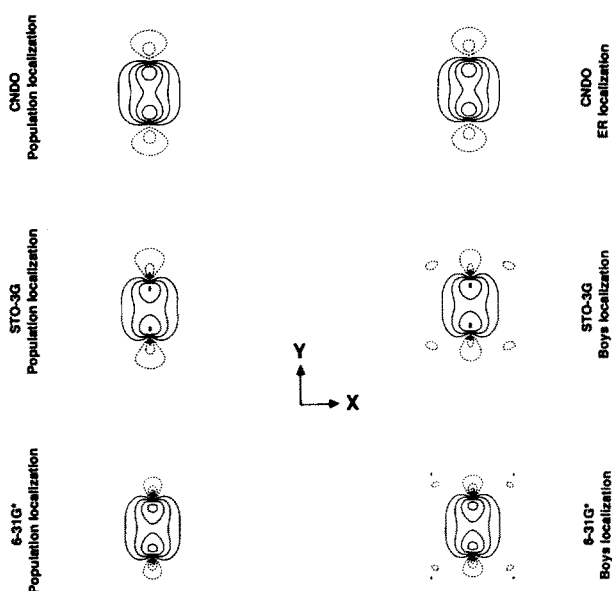


FIG. 7. The N–N single bond orbital of the  $N_2O_4$  molecule in various approximations. The contour lines indicate the same values as in Fig. 1.

calization may also lead to  $\pi$ -like orbitals lying in the plane of the molecule, this being the case of  $N_2O_4$ .

Finally, we have studied the convergence properties of all the three localization procedures using the method of consecutive two-by-two rotations. A complete cycle of  $N(N+1)/2$  two-by-two rotations for all pairs of occupied MOs was considered as an iteration step. For large enough  $l$  the behavior of the functional value  $G_l$  in the  $h$ th iteration was expected as

$$(G_{l+1} - G_\infty) \approx (G_l - G_\infty)^m, \quad (60)$$

where  $G_\infty$  is the converged value. Approximate linear convergence with  $m \approx 1$  was found in all cases. The estimated linear convergence speed factors  $h$  are summarized in Table IV. The convergence of the population localization method is similar to or slightly slower than that of the ER procedure but in most cases it is considerably faster than the convergence of the Boys method. These experiences suggest the possible application of the quadratically convergent iterative method of Leonard and Luken<sup>27</sup> for the determination of optimum population localized orbitals.

## VIII. SUMMARY

We have proposed here a localization method based on the minimization of an appropriately defined mean localization measure of the occupied molecular orbitals. The procedure does not require any additional quantities to be calculated beyond the atomic overlap integrals. It is suitable for separating core and valence orbitals and it has been shown that this procedure supports  $\sigma$ – $\pi$  separation. A numerical example demonstrates that this property has been approximately conserved for distorted molecular geometry. The resulting orbitals are almost identical to the Edmiston–Ruedenberg LOs and often more localized than their Boys counterparts. The algorithmic complexity of the method is

TABLE III. Values of localization functionals obtained for localized orbital sets calculated by various methods, and for canonical MOs.

		Localized MOs				Canonical MOs
	Functional		Population	ER	Boys	
CO	CNDO	$\mathcal{P}$	3.6920	3.6920		2.9939
		ER	3.3062	3.3062		3.1148
	STO-3G	$\mathcal{P}$	5.8346		5.7402	5.1818
		$B^1$	58.0601		65.0494	38.4268
	6-31G*	$\mathcal{P}$	5.9233		5.8229	5.4362
		$B^1$	60.7887		66.3735	45.5127
H <sub>2</sub> CO	CNDO	$\mathcal{P}$	3.9329	3.9296		2.5521
		ER	3.8680	3.8696		3.2165
	STO-3G	$\mathcal{P}$	6.0420		6.0030	4.8135
		$B^1$	132.6636		140.9499	45.4767
	6-31G**	$\mathcal{P}$	6.1341		6.0966	4.8204
		$B^1$	134.5438		142.0454	43.5313
B <sub>2</sub> H <sub>6</sub>	CNDO	$\mathcal{P}$	2.6759	2.6759		1.2046
		ER	2.8952	2.8952		2.0633
	STO-3G	$\mathcal{P}$	4.8171		4.8166	2.2020
		$B^1$	339.0476		339.1057	0.0
	6-31G**	$\mathcal{P}$	4.8898		4.8874	2.2013
		$B^1$	343.1215		343.2909	0.0
N <sub>2</sub> O <sub>4</sub>	CNDO	$\mathcal{P}$	12.4902	12.4712		3.3299
		ER	11.8746	11.8836		6.1303
	STO-3G	$\mathcal{P}$	18.4104		17.8455	5.4192
		$B^1$	4284.6297		4374.4829	0.0
	6-31G*	$\mathcal{P}$	18.9169		18.4036	5.3038
		$B^1$	4356.9356		4438.4344	0.0

TABLE IV. Number of iteration cycles required for convergence of the optimum functions up to eight decimal digits. Values  $h$  are the estimated linear convergence speed factors in Eq. (60).

		Population loc.		ER loc.		Boys loc.	
		No. it.	$h$	No. it.	$h$	No. it.	$h$
CO	CNDO	3	0.000 01	3	0.000 02		
	STO-3G	4	0.003			5	0.01
	6-31G*	3	0.000 003			5	0.03
H <sub>2</sub> CO	CNDO	3	0.002	3	0.002		
	STO-3G	4	0.001			6	0.01
	6-31G**	4	0.001			7	0.05
B <sub>2</sub> H <sub>6</sub>	CNDO	3	0.003	3	0.001		
	STO-3G	4	0.000 2			5	0.002
	6-31G**	4	0.000 5			4	0.002
N <sub>2</sub> O <sub>4</sub>	CNDO	5	0.03	4	0.02		
	STO-3G	8	0.06			9	0.08
	6-31G*	7	0.01			8	0.04

$N^3$  which is far more economical than the ER procedure and in this aspect is similar to the Boys localization. On the other hand, the speed of convergence is faster than that of the Boys iteration. The population localization can be used advantageously in large scale semiempirical and *ab initio* calculations.

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