Theoret. Chim. Acta (Berl.) 62, 107–132 (1982)

THEORETICA CHIMICA ACTA

Quadratically Convergent Calculation of Localized Molecular Orbitals

Joseph M. Leonard and William L. Luken

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, USA

Two iterative procedures for the transformation of canonical self-consistent field molecular orbitals to intrinsic localized molecular orbitals are proposed. A first-order method based on a series of $(n \times n)$ unitary transformations may be applied to orbitals which are far from convergence. The second method, based on Newton's method, yields quadratic convergence. Numerical results based on Boys' criterion are presented for water, carbon monoxide, boron fluoride, nitric oxide, and methylacetylene. A composite method may be used to obtain rapid convergence for large molecules for which it is not practical to calculate the entire hessian matrix. The performance of the composite method is demonstrated by application to the dinitrogen tetroxide molecule. Highly converged localized molecular orbitals may be obtained for most molecules with five to eight first-order iterations followed by three or four iterations based on either the second-order or composite method.

Key words: Localized orbitals – Molecular orbitals – Quadratic convergence.

1. Introduction

As noted by Fock, the properties of a single-determinantal many-electron wavefunction are invariant with respect to a unitary transformation among its orbitals [1]. Such a transformation is given by

$$\boldsymbol{\lambda} = \boldsymbol{U}\boldsymbol{\phi}, \tag{1}$$

with vectors $\boldsymbol{\lambda}$ and $\boldsymbol{\phi}$ each composed of a set of orthonormal spin orbitals. A single-determinantal wavefunction can be written as

$$\Phi = \hat{A}[\phi_1 \ \phi_2 \dots \phi_{n\alpha} \ \dots \ \phi_N], \tag{2}$$

where $\hat{A}$ is the N-electron antisymmetrizer and N is the number of electrons.

The spin-orbitals ϕ_i are defined as

$$\phi_i = f_i^{\alpha}\alpha \quad \text{for } i = 1 \text{ to } n_\alpha,$$

and

$$\phi_{i+n_\alpha} = f_i^{\beta}\beta \quad \text{for } i = 1 \text{ to } n_\beta, \tag{3}$$

where α and β are the $m_s = \pm 1/2$ spin functions and $n_\alpha + n_\beta = N$. The spatial functions f_i^s which minimize the energy of Φ are determined by the self-consistent field (SCF) equations [2, 4],

$$\hat{F}_s f_i^s = \sum_{j=1}^{m_s} \varepsilon_{ij}^s f_j^s \quad \text{for } i = 1 \text{ to } n_s, \text{ and } s = \alpha \text{ or } \beta. \tag{4}$$

For a closed shell Slater determinant, $\hat{F}_s$, f_i^s and ε_{ij}^s reduce to

$$\hat{F}_\alpha = \hat{F}_\beta = \hat{F}, \tag{5}$$

$$f_i^\alpha = f_i^\beta = f_i, \tag{6}$$

and

$$\varepsilon_{ij}^\alpha = \varepsilon_{ij}^\beta = \varepsilon_{ij}. \tag{7}$$

The canonical molecular orbitals (CMO's) are defined as those SCF orbitals, g_i^s, which diagonalize the Fock operator [3–5],

$$\langle g_i^s | \hat{F}_s | g_i^s \rangle = \varepsilon_{ij}^s = \varepsilon_i^s \delta_{ij}. \tag{8}$$

The CMO g_i^s is an eigenfunction of $\hat{F}_s$ with the eigenvalue ε_i^s. For a closed shell Slater determinant, this is given by

$$\hat{F} g_i = \varepsilon_i g_i. \tag{9}$$

Such orbitals are useful in the interpretation of molecular spectra [6, 7] and estimation of ionization potentials [8]. For closed-shell electronic configurations, CMO's reflect the symmetry of the irreducible representations of the molecular point group and therefore tend to be distributed through the entire molecule. Because of this delocalization, each spatial orbital g_i is a property of the entire molecule. If any part of the molecule changes, every CMO in the molecule may be affected. Consequently, it is difficult to compare the CMO's of one molecule to those of a related molecule.

Because of the invariance of Φ with respect to unitary transformations among its orbitals, it is possible to define alternatives to CMO's. If only transformations which associate orbitals of like spin are considered, the spatial functions of the alternative SCF orbitals of spin s are given by

$$\boldsymbol{f}^s = \boldsymbol{U}^s \boldsymbol{g}^s, \tag{10}$$

where $\boldsymbol{g}^s$ is composed of the CMO's associated with spin s and $\boldsymbol{U}^s$ is an $(n_s \times n_s)$ unitary matrix. This transformation can be used to produce orbitals each of which is concentrated in a relatively small part of the molecule [9–11]. The resulting localized molecular orbitals (LMO's) usually have the symmetries of reducible representations of the molecular point group. The elements of the transformation matrix $\boldsymbol{U}^s$ are determined by the set of starting orbitals $\{g_i^s\}$, and the criterion of localization. The spin index s will be suppressed in the following treatment.

Lennard-Jones and Hall demonstrated that localized orbitals could be determined for some molecules on the basis of symmetry principles alone [12–13]. These orbitals, called equivalent MO's, may be determined only for a few highly symmetric molecules. More generalized criteria are required to define LMO's for most molecules. Because all observable properties of a single determinantal molecular wavefunction are invariant to a unitary transformation, any such criterion must be based on a quantity which is not an observable property of the molecule.

The most commonly used criteria of localization are based on maximizing or minimizing a functional of the form

$$G = \sum_{i=1}^{n} (ii, ii), \tag{11}$$

where the definition of (ii, ii) depends on the criterion of localization. The possible choices for the quantity (ij, kl) include electronic repulsion integrals [5, 9]

$$(ij, kl) = \left\langle f_i(r_1) f_k(r_2) \left| \frac{1}{r_{12}} \right| f_j(r_1) f_l(r_2) \right\rangle, \tag{12}$$

for which the sum G is to be maximized. Another criterion defines LMO's as those orbitals which minimize the sum of orbital self-extension integrals [10, 14–15]. In this case, (ij, kl) may be defined as either

$$(ij, kl) = \langle f_i(r_1) f_k(r_2) | r_{12}^2 | f_j(r_1) f_l(r_2) \rangle, \tag{13a}$$

or

$$(ij, kl) = \langle f_i | \vec{r} | f_j \rangle \cdot \langle f_k | \vec{r} | f_l \rangle. \tag{13b}$$

A third criterion involves maximization of the orbital self-overlap of charge density [9, 11], for which

$$(ij, kl) = \langle \phi_i(r_1) \phi_k(r_2) | \delta(r_{12}) | \phi_j(r_1) \phi_l(r_2) \rangle. \tag{14}$$

Localized orbitals obtained from any of these criteria have several useful features: they can usually be interpreted in terms of a Lewis or Linnett [16] structure and most LMO's are concentrated on one or two atoms. This facilitates the partitioning of molecules into fragments, providing a basis for treating molecular properties in terms of distinct functional groups [17–18]. The idea of functional groups can be used in a quantitative sense by the construction of molecular wavefunctions from the wavefunctions of suitable fragments [19–25]. Considerable attention has been devoted to the use of LMO's in the study of electron correlation [26–28].

Each of these criteria defines a specific set of LMO's. In addition, recent work has shown a close connection between LMO's and the Fermi hole [29]. The problem remains of finding the set of orbitals which satisfy a specific criterion. In some cases, especially with the self-repulsion and density criteria, this process can be more difficult than the solution of the SCF equations (in terms of computational effort). This situation may limit the utility of the concept of LMO's.

This paper presents a quadratically convergent method for finding orbitals which satisfy a criterion of localization. The next section briefly reviews the techniques previously developed for determining LMO's. The third section presents the principal methods developed in this work. The fourth section presents results obtained from application of these methods to water, carbon monoxide, boron fluoride, nitric oxide, methylacetylene, and dinitrogen tetroxide molecules.

2. Previous Developments

In principle, there exists a unitary transformation relating a delocalized set of orbitals (CMO's for example) to a localized set. The general functional form of this transformation is unknown. As a result, several iterative procedures have been developed based on series of unitary transformations, each increasing the degree of localization of the set of orbitals.

The transformation performed each iteration is given by

$$\boldsymbol{f}^{(I+1)} = \boldsymbol{u}^{(I)}\boldsymbol{f}^{(I)}, \tag{15}$$

where $\boldsymbol{f}^{(I+1)}$ is composed of the more-localized orbitals. Edmiston and Ruedenberg proposed an iterative scheme based on a sequence of pairwise rotations [9]. In this approach, the matrix $\boldsymbol{u}^{(I)}$ is given by $\boldsymbol{u}_{ij}$, where

$$(u_{ij})_{kl}\begin{cases} =1 & k=l\neq i \text{ or } j \\ =\cos\alpha_{ij} & k=l=i \text{ or } j \\ =\sin\alpha_{ij} & k=i>l=j \\ =-\sin\alpha_{ij} & k=i<l=j \\ =0 & \text{otherwise.} \end{cases} \tag{16}$$

The matrix $\boldsymbol{u}_{ij}$ can be redefined in terms of the product

$$\boldsymbol{u}_{ij} = \boldsymbol{V}_{ij}\boldsymbol{T}_{ij}, \tag{17}$$

where the elements of $\boldsymbol{T}_{ij}$ are given by

$$(T_{ij})_{kl}\begin{cases} =1 & k=l \\ =\tan\alpha_{ij} & k=i>l=j \\ =-\tan\alpha_{ij} & k=i<l=j \\ =0 & \text{otherwise.} \end{cases} \tag{18}$$

The matrix $\boldsymbol{V}_{ij}$ is given by

$$\boldsymbol{V}_{ij} = (\boldsymbol{T}_{ij}^{\dagger}\boldsymbol{T}_{ij})^{-1/2}, \tag{19}$$

with elements

$$(V_{ij})_{kl}\begin{cases} =1 & k=l\neq i \text{ or } j \\ =\cos\alpha_{ij} & k=l=i \text{ or } j \\ =0 & \text{otherwise.} \end{cases} \tag{20}$$

The rotation angle which maximizes the increase in the degree of localization of the (i, j) pair of orbitals is given by [9, 30]

$$\alpha_{ij} = \tan^{-1}(-B_{ij}/A_{ij})/4, \tag{21}$$

where A_{ij} and B_{ij} are determined by

$$A_{ij} = (ij, ij) - [(ii, ii) + (jj, jj) - 2(ii, jj)]/4 \tag{22}$$

and

$$B_{ij} = (ii, ij) - (ij, jj). \tag{23}$$

Each pairwise rotation increases the degree of localization of the pair of orbitals (f_i, f_j) by D_{ij}, where D_{ij} is given by

$$D_{ij} = A_{ij} + (A_{ij}^2 + B_{ij}^2)^{1/2}. \tag{24}$$

The sequence of (i, j) rotations is repeated until all values of D_{ij} approach zero. From the definition of D_{ij}, it follows that LMO's possess the properties $A_{ij} < 0$ and $B_{ij} = 0$ [9].

The major part of the effort involved in determining localized orbitals by this type of approach is the effort required to calculate the appropriate integrals over orbitals. This problem is especially severe for the energy (Eq. (12)) and density (Eq. (14)) criteria. As such, it is essential to minimize the number of times these integrals must be recalculated.

The matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ determine $n/2$ independent pairwise rotations. The results of performing a set of such rotations depend on the choice of the rotations and the order in which the rotations are performed. Alternatively, it is possible to perform all $n(n-1)/2$ rotations determined by the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$. In this method, a partially transformed pair of orbitals (f_i', f_j') may be rotated by an angle α_{ij} determined by the unrotated pair (f_i, f_j). If the angles of rotation are small, then the errors introduced by using such incorrectly determined rotation angles are also small. However, if the rotation angles are large, the entire (2×2) rotation method is so crude that no serious damage is done by performing all possible rotations. Consequently, the pairwise rotation method based on all $n(n-1)/2$ pairwise rotations has been found to converge more rapidly than the method based on the $n/2$ independent pairwise rotations [5].

As an alternative to methods based on pairwise rotations, it is also possible to develop iterative methods based on $(n \times n)$ unitary transformations. The first such method was proposed by Edmiston and Ruedenberg [9]. They proposed that the transformation matrix be defined as

$$\boldsymbol{u}_G^{(I)} = \exp(\varepsilon \boldsymbol{B}), \tag{25}$$

where $\boldsymbol{B}$ is proportional to the gradient of the localization criterion with respect to the transformation matrix and ε is a scalar constant. In the limit of small ε or $\boldsymbol{B}$, this reduces to

$$\boldsymbol{u}_G^{(I)} = \boldsymbol{I} + \varepsilon \boldsymbol{B}. \tag{26}$$

Edmiston and Ruedenberg originally suggested that the scalar ε be determined by trial and error. Taylor proposed that ε be determined by [31]

$$\varepsilon = -B^2/2J_2, \tag{27}$$

where J_2 is determined by the second derivative of the criterion of localization with respect to ε.

This transformation is based on the method of steepest ascents [31]. As such, it concentrates on the most highly determined elements of the transformation matrix, and performs very poorly with respect to the weakly determined elements. Consequently, such methods may require a large number of iterations to optimize a set of LMO's. In numerical implementation of Eq. (27) it was found that this method performed poorly on molecules such as methylacetylene [32].

Another $(n \times n)$ transformation scheme, called the eigenvector method, has also been proposed and tested [32]. This method resembles Taylor's method except that the gradient vector $\boldsymbol{B}$ is replaced with an eigenvector $\boldsymbol{V}$ of the corresponding Hessian matrix, and ε may be determined by the eigenvalue associated with $\boldsymbol{V}$. Transformations based on Fletcher–Reeves and Fletcher–Powell methods have also been investigated [33, 34]. These methods did not demonstrate any clear advantage over the steepest ascent method.

As an alternative to the techniques described above, it is also possible to determine localized orbitals directly from the SCF equations using a modified Fock operator [9, 35, 36]. This direct method eliminates the need to transform canonical orbitals into localized orbitals. However, numerical tests of this direct method have been characterized by convergence problems [37]. Localized orbitals are also determined by the generalized valence bond (GVB) method and other methods based on strongly orthogonalized geminals [38, 39] or non-orthogonal orbitals [40]. These methods have the advantage of determining LMO's for correlated wavefunctions. However, they involve specialized MC-SCF methods and tend to require much more computational effort than the methods discussed here.

3. Second-Order $(n \times n)$ Transformations

The $(n \times n)$ unitary matrix transforming a less-localized set of orbitals to a more-localized set can be written as

$$\boldsymbol{U} = \boldsymbol{W}\boldsymbol{R}, \tag{28}$$

where $\boldsymbol{W}$ is the positive definite matrix given by

$$\boldsymbol{W} = (\boldsymbol{R}\boldsymbol{R}^{\dagger})^{-1/2}. \tag{29}$$

The matrix $\boldsymbol{R}$ will be defined as

$$\boldsymbol{R} = \boldsymbol{N}\boldsymbol{T}, \tag{30}$$

where

$$\boldsymbol{T} = \boldsymbol{I} + \boldsymbol{t} \tag{31}$$

and $\boldsymbol{t}$ is an antisymmetric matrix

$$\boldsymbol{t}^{\dagger} = -\boldsymbol{t}. \tag{32}$$

The matrix $\boldsymbol{N}$ is a diagonal matrix which normalizes the columns of $\boldsymbol{R}$. Thus,

$$N_{ij} = (\Sigma_k T_{ki}^2)^{-1/2}\delta_{ij}. \tag{33}$$

The unitary matrix $\boldsymbol{U}$ is completely determined by the $n(n-1)/2$ independent off-diagonal elements of $\boldsymbol{T}$. This can be used to construct a vector $\boldsymbol{t}$ with elements $t_I = t_{ij}$, where $I = j + i(i-1)/2$ for $i > j$.

Application of the transformation $\boldsymbol{U}$ to an orthonormal set of orbitals $\{f_1, \ldots f_n\}$ produces a set of orthonormal orbitals $\{f'_1, \ldots f'_n\}$ given by

$$\boldsymbol{f}' = \boldsymbol{Uf}. \tag{34}$$

The new value of the localization criteria, G', can be obtained as

$$G' = \sum_{i=1}^{n} (i'i'|i'i'). \tag{35}$$

This can be expanded in terms of the quantities t_{ij}, given as

$$G' = G_0 + \Sigma_I t_I G_1(I) + \Sigma_{I,J} t_I t_J G_2(I, J) \tag{36}$$

to second order. The terms in G' are given as

$$G_0 = \sum_{i=1}^{n} (ii, ii), \tag{37}$$

which is the value of the localization criterion prior to any transformation,

$$G_1(I) = G_1(ij) = 4B_{ij}, \tag{38}$$

which is the gradient of the localization criterion with respect to the elements t_{ij}, and $G_2(I, J) = G_2(ij, kl)$, which is proportional to the matrix of second derivatives (the hessian matrix). The diagonal elements of $\boldsymbol{G}_2$ are given by

$$G_2(ij, ij) = 8A_{ij}, \tag{39}$$

and the off-diagonal terms of $\boldsymbol{G}_2$ are given by [32]

$$\begin{aligned} G_2(ij, kl) = {} & [4(ij, il) + 2(ii, jl) - (jj, jl) - (ll, lj)]\delta_{ik} \\ & + [4(ij, jk) + 2(jj, ik) - (ii, ik) - (kk, ki)]\delta_{jl} \\ & - [4(ij, jl) + 2(jj, il) - (ii, il) - (ll, li)]\delta_{jk} \\ & - [4(ij, ik) + 2(ii, jk) - (jj, jk) - (kk, kj)]\delta_{il} \end{aligned} \tag{40}$$

for $(ij) \neq (kl)$.

In the limit of small rotations ($|t_{ij}| \approx 0$), the ($n \times n$) steepest ascent transformation proposed by Edmiston and Ruedenberg [9] and Taylor [31] can be written as

$$\boldsymbol{t}_1 = \varepsilon \boldsymbol{G}_1/4. \tag{41}$$

To obtain a quadratically convergent iterative procedure, the elements of the transformation matrix, $\boldsymbol{t}$, should be determined by the corresponding elements of the vector

$$\boldsymbol{t}_2 = -\boldsymbol{G}_2^{-1}\boldsymbol{G}_1/2. \tag{42}$$

However, two problems are associated with the use of this equation to determine the transformation matrix $\boldsymbol{t}$. First, the number of elements contained in the hessian matrix $\boldsymbol{G}_2$ is on the order of n^4 (where n is the number of orbitals present in the set being considered). The presence of the delta functions in the definition of $\boldsymbol{G}_2$ reduces the number of non-zero matrix elements to something on the order of n^3. Even so, the dimensions of $\boldsymbol{G}_2$ make it somewhat inconvenient to manipulate. In addition, for the energy [5, 9] and density [9, 11] criteria, the functional (ij, kl) requires three-index integrals which are not required for any of the (2 × 2) rotation schemes. The computational effort required to determine these integrals is not inconsiderable, and the large number of these integrals can often be inconvenient to manipulate. These two problems can be avoided by the approximate method described below.

If the off-diagonal elements of $\boldsymbol{G}_2$ are neglected, the transformation matrix, $\boldsymbol{t}$, is given by

$$\begin{aligned} t_a(ij) &= -G_1(ij)/2G_2(ij, ij) \\ &= -B_{ij}/4A_{ij}. \end{aligned} \tag{43}$$

This can be modified to give

$$t'_a(ij) = \tan(\alpha_{ij}) \tag{44}$$

for $i \neq j$ and α_{ij} determined by Eq. (21). For the case of only two orbitals to be localized, this is identical to the pairwise rotation scheme of Edmiston and Ruedenberg. When the number of orbitals present is greater than two, the ($n \times n$) transformation determined by Eq. (44) is equivalent to performing all of the possible pairwise rotations simultaneously. This is in contrast to the conventional method in which all possible (2 × 2) rotations are performed sequentially. Unlike the sequential (2 × 2) rotation scheme, which preserves orthonormality at every step, the transformation matrix, $\boldsymbol{T}$, determined by Eqs. (31) and (44) is not unitary. Instead, application of Eq. (28)–(30) determines a unitary matrix, $\boldsymbol{U}$, which yields an orthonormal set of orbitals most closely resembling (in an RMS sense) those determined by application of $\boldsymbol{T}$ [41].

The conventional procedure used to convert the transformation matrix $\boldsymbol{T}$ to the unitary matrix $\boldsymbol{U}$ is based on diagonalizing the matrix $\boldsymbol{R}\boldsymbol{R}^+$ to determine $\boldsymbol{W}$ defined by Eq. (29). Such a procedure, however, may yield a matrix $\boldsymbol{W}' = \boldsymbol{V}\boldsymbol{W}$ where $\boldsymbol{V}$ is an arbitrary unitary matrix and $\boldsymbol{W}'$ is not positive definite. In order to avoid this problem, as well as to avoid the need to calculate the eigenvalues and eigenvectors of $\boldsymbol{RR}^+$, we have developed an iterative power series method which is described in the Appendix.

The need to convert the transformation matrix $\boldsymbol{T}$ to a unitary matrix represents an extra computational burden not shared by conventional 2×2 methods. Our experience, based on use of the iterative power series method described in the Appendix, indicates that this is not a serious problem. Alternative methods based on 2×2 transformations have also been proposed [42].

In the limit of very small rotation angles, α_{ij}, the transformation determined by Eq. (44) becomes equivalent to that obtained by the use of sequential (2×2) rotations. Consequently, the convergence properties of this approximate $(n\times n)$ method are identical to those of the conventional pairwise schemes. As will be shown later, the rate of convergence can be considerably improved through the use of Eq. (42). This transformation, however, does not lead to a properly localized set of orbitals unless all of the eigenvalues of the hessian matrix, $\boldsymbol{G}_2$, are non-positive. Because of this, such a transformation may not be applied directly to the canonical orbitals.

In practice, a two-step procedure has been found to be effective. First, the transformation determined by Eq. (44) is used until all values of A_{ij} (the diagonal elements of $\boldsymbol{G}_2$) are negative. At this point (or following a small number of further iterations), the transformation determined by Eq. (42) is used. Quadratic convergence is then obtained.

The most serious drawback to the second order method described here is the effort required to calculate and manipulate the Hessian matrix. The order of this matrix is $n(n-1)/2$, where n is the number of orbitals to be localized. Consequently, this matrix contains on the order of n^4 elements determined by Eqs. (39) and (40). Because of the delta functions in Eq. (40), the number of non-zero matrix elements is only proportional to n^3. In spite of this, the need to calculate on the order of n^3 two-electron integrals not required by the first order methods represents a large burden which may render this method impractical for the energy [5, 9] and density [9, 11] criteria.

In the case of the orbital centroid criterion [10, 14, 15], all two-electron integrals are determined by products of one-electron dipole integrals. The first order methods all require $3n(n+1)/2$ dipole integrals over molecular orbitals. The second order method described here requires no additional integrals not required by first order methods. Consequently very little additional effort is required to calculate the Hessian matrix.

The following sections report the results of calculations on water, carbon monoxide, boron fluoride, nitric oxide, methylacetylene, and dinitrogen tetroxide. Because of the factors cited above, all of these results are based on the orbital centroid criterion of Boys [10, 14, 15]. In spite of the advantages offered by this criterion, the large size of the Hessian matrix can become an obstacle to the practical application of the second order method to large molecules. Consequently, we introduce a subset localization method for the N_2O_4 calculations which demonstrate how to obtain rapid, though not second order, convergence for large molecules.

4. Results

1. *Water*

The convergence behavior of the transformation determined by Eqs. (42) and (44) is demonstrated in Table 1. These results were obtained from the application of the Boys criterion (Eq. (13)) to the canonical SCF molecular orbitals of the water molecule. The orbitals are based on the standard Huzinaga–Dunning double-zeta (DZ) basis set [43] and the geometry of Laidig et al. [44].

The convergence of this procedure may be characterized by any of several quantities. One of these is $D_{\max}$, the maximum value of D_{ij} defined by Eq. (24). This represents the maximum increase in the degree of localization obtainable by performing a single pairwise rotation. Near convergence, the value of D_{ij} may be approximated as

$$D_{ij} \approx -B_{ij}^2/2A_{ij}. \qquad (45)$$

Table 1. Convergence of localization procedures for the water molecule. These results are based on double-zeta SCF molecular orbitals. The first-order results are based on Eq. (44) and the second-order results are based on Eq. (42). $D_{\max}$ indicates the maximum value of D_{ij} defined by Eq. (24) and T_{rms} is the rms off-diagonal transformation matrix element, Eq. (47). The values of $D_{\max}$ and T_{rms} are determined prior to the transformation. The first iteration starts with the canonical SCF orbitals

First Order			Second Order		
iteration	$D_{\max}$	T_{rms}	iteration	$D_{\max}$	T_{rms}
1	1.3746410	0.6750231[a]		—	—
2	0.2223017	0.2602457[a]		—	—
3	0.0875848	0.2476258[a]		—	—
4	0.0107877	0.0523173		—	—
5	0.0023628	0.0265749		—	—
6	0.0008162	0.0156787		—	—
7	0.0002821	0.0096118	1	0.0002821	0.007303
8	0.0001020	0.0057982	2	1.30×10^{-9}	2.07×10^{-5}
9	0.0000374	0.0035681	3	3.23×10^{-18}	1.04×10^{-9}
10	0.0000139	0.0021768			
	⋮	⋮			
15	1.04×10^{-7}	1.89×10^{-4}			
20	7.84×10^{-10}	1.65×10^{-5}			
25	5.95×10^{-12}	1.44×10^{-6}			

[a] Some diagonal elements of the hessian matrix are positive.

A closely related measure of the progress towards convergence is given by the root mean square off-diagonal element of the transformation matrix

$$T_{rms} = \left[\sum_{i \neq j} (T_{ij})^2 / n(n-1) \right]^{1/2}, \tag{46}$$

where n is the number of orbitals being localized. In the case of the transformation determined by Eq. (44), this may be approximated by

$$T_{rms} \approx \left[\sum_{i \neq j} (B_{ij}/4A_{ij})^2 / n(n-1) \right]^{1/2} \tag{47}$$

as the rotation angles, α_{ij}, become small. As shown in Table 1, this exhibits essentially linear convergence.

The rate of convergence may be considerably accelerated by the use of the transformation defined by Eq. (42). This method, however, cannot be applied until all of the eigenvalues of the hessian matrix, $\boldsymbol{G}_2$, are negative. A necessary but not sufficient condition for the eigenvalues of $\boldsymbol{G}_2$ to be negative is for all of the diagonal elements of $\boldsymbol{G}_2$ to be negative. These are determined by the values of A_{ij} for $i \neq j$. Consequently, calculation of the off-diagonal portions of the hessian may be delayed until the values of A_{ij} are all negative. At this point, the highest eigenvalue of the hessian may be calculated to determine if it is positive. If it is, the first-order transformation of Eq. (44) can be repeated until this eigenvalue becomes either zero or negative. Usually, it is not necessary to determine this eigenvalue on subsequent iterations once it has been found to be zero or negative. In order to avoid premature calculation of the hessian matrix, the first-order transformation is performed for a small number of iterations after all values of A_{ij} are found to be negative.

Application of this procedure is illustrated in Table 1. In this case, all values of A_{ij} were negative after three iterations based on Eq. (44). Three additional first-order transformations were performed to avoid premature calculation of the hessian matrix. Three further iterations based on Eq. (42) yielded fully

Table 2. Molecular geometry and locations of orbital centroids of the LMO's for water. These results are based on the orbital centroid criterion and a double-zeta atomic orbital basis set. All results are reported in atomic units

Atom/Orbital	X	Y	Z
Oxygen	0.0	0.0	0.0
Hydrogen-1	0.0	1.515263	1.049898
Hydrogen-2	0.0	−1.515263	1.049898
0-1s	0.0	0.0	0.000387
0-H1	0.0	0.790863	0.595310
O-H2	0.0	−0.790863	0.595310
0-*lp*1	0.497437	0.0	−0.324101
0-*lp*2	−0.497437	0.0	−0.324101

converged localized orbitals. These calculations required 4.13 minutes on a PDP-11/44 computer. The first order method, used alone, required 26 iterations (9.58 minutes) to reach T_{rms} less than 10^{-6}.

Table 2 indicates the molecular geometry used for this calculation, along with the location of the centroids of the resulting localized orbitals. As expected, these have the forms of an oxygen inner-shell orbital, two O—H σ-bonds and two oxygen lone-pairs. The H—O—H bond angle used is 110.6° and the angle determined by the orbital centroids of the two σ-bonds is 106.1°. The angle between the two lone-pair centroids is 113.8°. These results are in good agreement with those previously obtained by von Niessen [45].

4.2. Carbon Monoxide

The locations of the centroids for the localized orbitals of carbon monoxide, as determined by the orbital centroid criterion, are shown in Table 3. The molecular geometry, double-zeta basis set and starting SCF orbitals were taken from the published tabulation of Snyder and Basch [46]. The LMO's have the form of

Table 3. Molecular geometry and locations of orbital centroids of the LMO's of CO and BF. These results are based on the orbital centroid criterion and a double-zeta atomic orbital basis set. All results are reported in atomic units

	Carbon Monoxide		
Atom/Orbital	X	Y	Z
Carbon	0.0	0.0	0.0
Oxygen	0.0	0.0	2.132
Carbon-1*s*	0.0	0.0	0.000870
Oxygen-1*s*	0.0	0.0	2.131475
C—O τ1	0.347103	0.346354	1.514695
C—O τ2	−0.473503	0.127423	1.514695
C—O τ3	0.126400	−0.473777	1.514695
Carbon-*lp*	0.0	0.0	−0.767322
Oxygen-*lp*	0.0	0.0	2.696387

	Boron Fluoride		
Atom/Orbital	*X*	*Y*	*Z*
Boron	0.0	0.0	−1.195267
Fluorine	0.0	0.0	1.195267
Boron-1*s*	0.0	0.0	−1.194107
Fluorine-1*s*	0.0	0.0	1.195078
Fluorine-*lp*1	−0.346203	−0.346203	1.268829
Fluorine-*lp*2	0.472923	−0.126719	1.268829
Fluorine-*lp*3	−0.126719	0.472923	1.268829
B—F bond	0.0	0.0	0.518928
Boron-*lp*	0.0	0.0	−2.040630

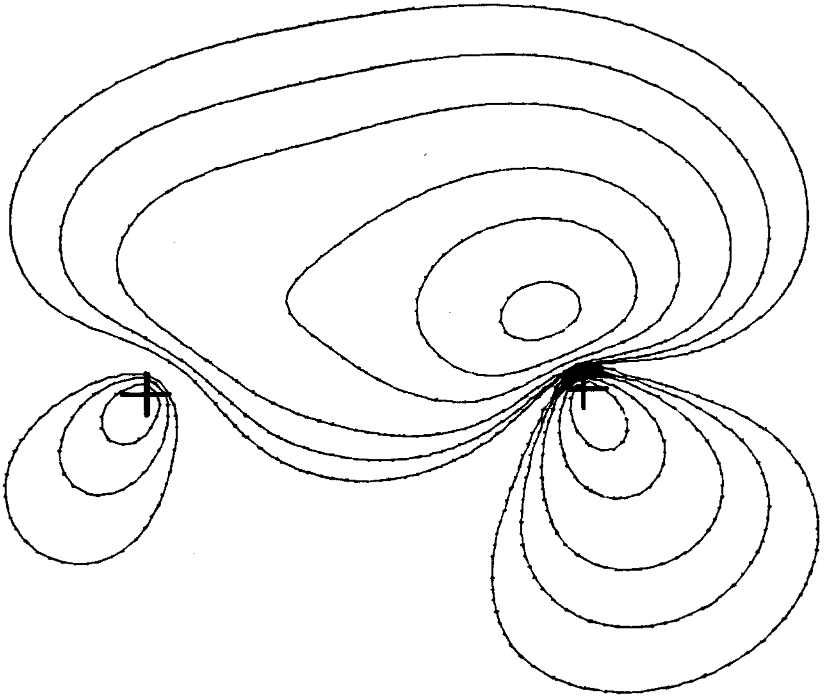

Fig. 1. One of the three equivalent localized molecular orbitals comprising the carbon-oxygen triple bond of carbon monoxide. The contour levels shown here indicate densities of 0.01, 0.02, 0.04, 0.1, 0.2, and 0.4 electrons per cubic bohr starting from the outermost contour. The oxygen nucleus is on the right

an inner-shell orbital and a lone-pair orbital on each atom, with a set of three equivalent C—O τ-bonds. The shape of one of the τ-bonds is illustrated in Fig. 1.

In this molecule, rotation of the three τ-bonds about the internuclear axis produces no change in the degree of localization obtained. Because of this continuous degeneracy [47], one of the eigenvalues of the hessian matrix, $\boldsymbol{G}_2$, is zero and Eq. (42) is indeterminant. Prior to convergence, this eigenvalue is found to be positive, and it asymptotically approaches zero as the orbitals converge to the localized results.

In order to apply Eq. (42) to a molecule with continuous degeneracy, the order of $\boldsymbol{G}_1$ and $\boldsymbol{G}_2$ may be reduced by striking out the row(s) and column(s) corresponding to the component of largest magnitude of each eigenvector with a nonnegative eigenvalue. The corresponding element(s) of the transformation matrix, $\boldsymbol{T}$, are set to zero. As shown in Table 4, a small number of such modified second-order transformations (2–3) following five based on Eq. (44) are sufficient to obtain well-converged localized orbitals for carbon monoxide. These results are in good agreement with the results of von Niessen [45].

Table 4. Convergence behavior of first and second-order localization transformations. The number of zeros specifies the number of eigenvalues of the hessian matrix which equal zero and $\lambda_{\min}$ is the smallest non-zero eigenvalue. All results are based on the orbital centroid criterion

	No. of iterations					
Atom	1st-order	2nd-order	T_{rms}	No. zeros	$\lambda_{\min}$	Time[a]
CO	25	0	8.0×10^{-6}	—	—	19.40
	5	3	$<10^{-8}$	1	−0.589081	7.50
BF	156	0	9.7×10^{-5}	—	—	118.60
	6	5	$<10^{-8}$	1	−0.050119	14.05
$NO(^2\Pi)\alpha$	13	0	4.0×10^{-6}	—	—	15.06
	5	3	$<10^{-8}$	0	−0.692965	11.27
$NO(^2\Pi)\beta$	250	0	6.5×10^{-5}	—	—	171.82
	8	6	$<10^{-8}$	0	−0.002371	14.19
$NO(^2\Sigma)\alpha$	15	0	8.0×10^{-6}	—	—	17.44
	5	3	$<10^{-8}$	2	−0.541528	11.27
$NO(^2\Sigma)\beta$	36	0	9.0×10^{-6}	—	—	24.81
	5	4	$<10^{-8}$	1	−0.570891	6.72
C_3H_4	250	0	2.0×10^{-4}	—	—	299.06
	5	4	$<10^{-8}$	0	−0.011263	18.26
	5	4	$<10^{-8}$	0	+0.014770	18.32[b]
	0	4	$<10^{-8}$	0	−0.010669	13.24[c]
N_2O_4	27	0	5.4×10^{-7}	—	—	870.61
	9	6[d]	5.8×10^{-7}	0	−0.483466	568.43

[a] Time required for localization on a PDP-11/44, in minutes.
[b] Saddle-point.
[c] Convergence from eigenvector transformation (Eq. (48)) following convergence to a saddle-point.
[d] Twelve MO subset used to calculate the hessian matrix.

4.3. Boron Fluoride

Boron fluoride, like the isoelectronic molecular carbon monoxide, has a zero eigenvalue of the hessian matrix. Unlike CO, for which the vanishing eigenvalue is associated with a C—O triple bond, the zero eigenvalue for BF is associated with a set of three equivalent lone-pair orbitals on fluorine. As shown in Fig. 2, each of these fluorine lone-pairs involves significant contribution from the region of the boron atom. Consequently, the B-F-centroid angle formed by each of these orbitals is only 98.5° instead of 109.5° expected for idealized sp^3 hybrid orbitals. The angle between the B—F axis and the point of maximum density in each of these orbitals is 107.5°, indicating that the location of the orbital centroid reflects fluorine to boron delocalization rather than a large degree of rehybridization. This delocalization or "back-bonding" apparently increases the effective B—F bond order, resulting in a B—F bond which is 0.084 bohr shorter than that found in BF_3 [48].

As shown in Table 4, the first-order $(n\times n)$ localization procedure converged much more slowly for BF than for CO. This sluggish convergence is caused by a relatively small eigenvalue (−0.050) of the hessian matrix. For this case,

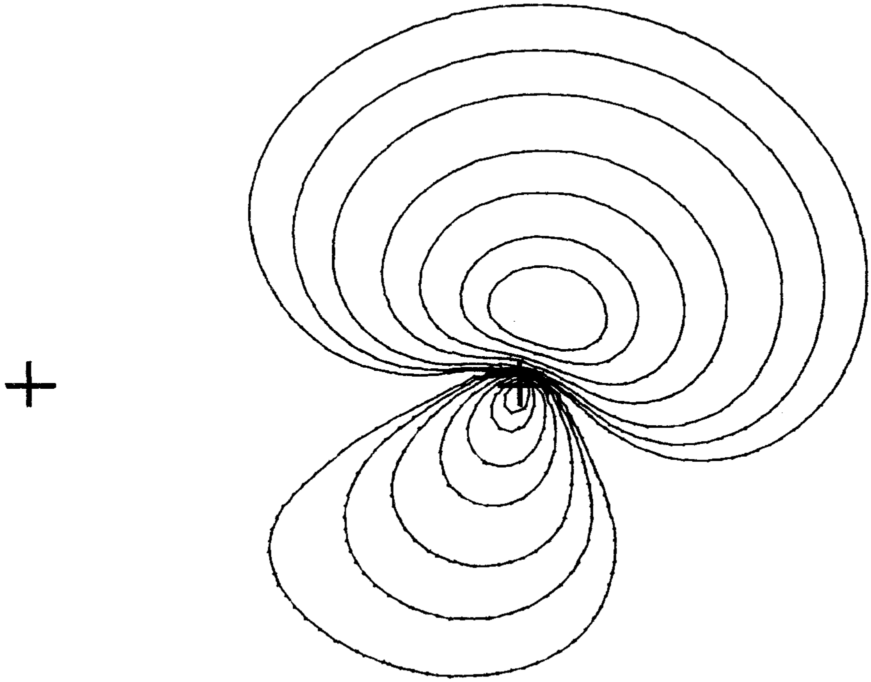

Fig. 2. One of the three equivalent localized molecular orbitals representing the fluorine lone pairs in boron fluoride. The density contours shown here include 0.6 electrons per cubic bohr in addition to those occurring in Fig. 1. The fluorine nucleus is on the right

activation of the second-order procedure following six first-order iterations yielded rapid convergence to the final localized orbitals. The resulting centroids are provided in Table 3.

4.4. Nitric Oxide

Nitric oxide is a diatomic molecule with an odd number of electrons. In addition, the $^2\Pi$ ground state has a half-filled set of π orbitals, giving the state open-shell character with respect to spatial coordinates as well as electronic spin. The current work is based on two unrestricted SCF wavefunctions: one for the $(5\sigma)^2(1\pi)^4(2\pi\alpha)^2\Pi$ ground state, and one for the $(5\sigma\beta)(1\pi)^4(2\pi\alpha)^2\,{}^2\Sigma$ excited state, both using the 6-31G basis set [49] with eight orbitals occupied by α spin electrons and seven orbitals occupied by β spin electrons. The sets of α spin and β spin orbitals for each state were each localized separately, yielding α-LMO's and β-LMO's [50].

The orbital centroids determined in these calculations are presented in Table 5. The centroids of the $^2\Pi$ state fit the pattern expected on the basis of Linnett's theory [16]. Because of the unfilled 2π orbital, the hessian matrix for the α-LMO's has no zero eigenvalues. The hessian matrix for the β-LMO's has one small non-zero eigenvalue which reflects the inequivalence of the $1\pi_x$ and $1\pi_y$

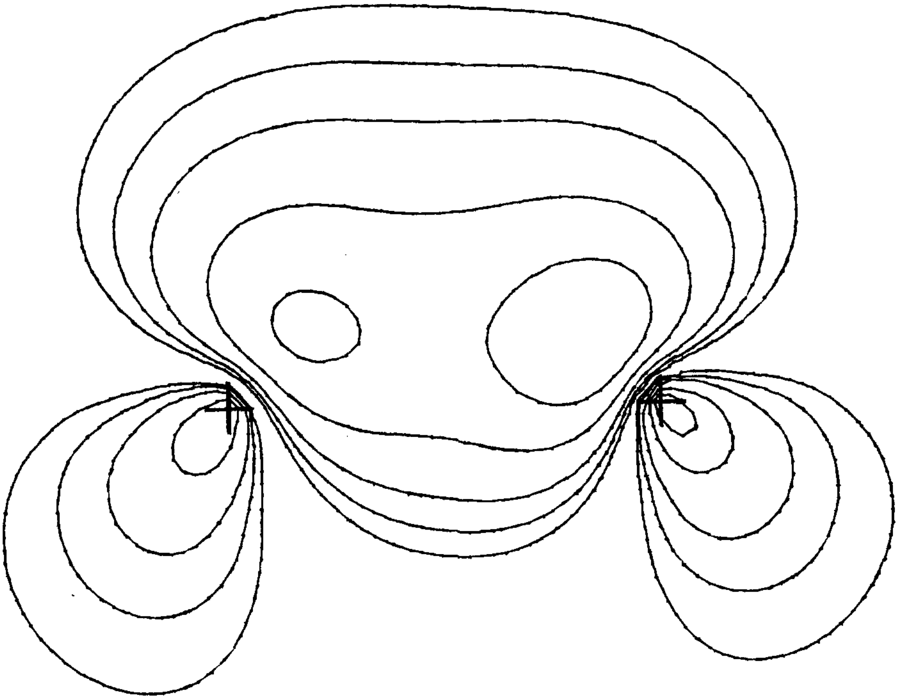

Fig. 3. One of two equivalent α-localized molecular orbitals comprising the nitrogen-oxygen double bond in the $^2\Pi$ electronic state of nitric oxide. The density contours are specified in Fig. 1. The oxygen nucleus is on the right

canonical molecular orbitals in this wavefunction. The corresponding eigenvalue equals zero in the $^2\Sigma$ electronic state where the $1\pi_x$ and $1\pi_y$ orbitals are related by a 90° rotation.

In the case of the α-LMO's, promotion of one electron from the 5σ (bonding) to the 2π (antibonding) orbital decreases the α bond order from one to zero. This is reflected in a dramatic change in the forms of the α-LMO's in the $^2\Sigma$ state compared to the $^2\Pi$ state. The eight α-LMO's of the $^2\Sigma$ state consist of two inner-shell orbitals and two sets of three equivalent orbitals. Each of the six valence LMO's is essentially an sp^2 hybrid orbital oriented perpendicular to the internuclear axis. Each of these sets can be independently rotated about the bond axis, resulting in two zero eigenvalues of the hessian matrix. A comparison of a $^2\Pi$ bonding LMO and a $^2\Sigma$ non-bonding LMO is presented in Figs. 3 and 4. In this case, the order of the hessian matrix was reduced by two by striking out the two rows and columns corresponding to the largest components of the eigenvectors with eigenvalues of zero.

4.5. *Methylacetylene*

As noted in the preceding section, the α-LMO's for the $^2\Sigma$ electronic state of NO include two sets of three equivalent orbitals, and each set may be rotated

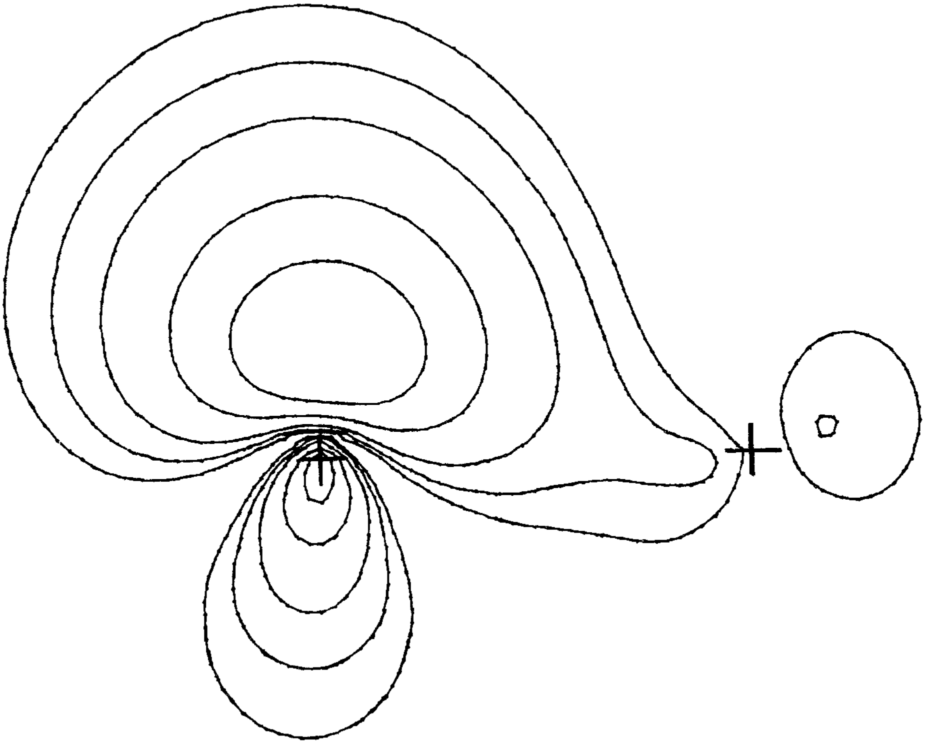

Fig. 4. One of the three equivalent α-localized molecular orbitals representing the non-bonding electrons on the nitrogen atom in the $^2\Sigma$ electronic state of nitric oxide. The density contours are specified in Fig. 1

independently of the other without changing the degree of localization. A similar situation occurs in methylacetylene, which has a set of three equivalent C—H bonds in the methyl fragment and a set of three equivalent τ-bonds in the acetylene fragment. The location of the protons determine the orientation of the C—H bond orbitals. In addition, the degree of localization is weakly dependent on the orientation of the τ-bonds relative to the C—H bonds. Consequently, methylacetylene has no zero eigenvalues, but one of the non-zero eigenvalues is very small.

The small non-zero eigenvalue, which is responsible for the orientation of the τ-bonds with respect to the C—H bonds, causes severe convergence difficulties for the first-order transformation, including conventional methods based on (2×2) rotations as well as the $(n \times n)$ transformation determined by Eq. (44). Thus Kleier et al. [32] required over 200 iterations to satisfy their convergence criterion. As indicated in Table 4, over 250 iterations based on Eq. (44) are required to reduce T_{rms} to less than 10^{-4}. The first few iterations for these calculations proceed very well, with a rapid increase in the localization sum. After approximately ten iterations, the orbitals are all close to their final forms,

Table 5. Molecular geometry and locations of orbital centroids of the LMO's for the $^2\Pi$ and $^2\Sigma$ states of NO. These results are based on the orbital centroid criterion and a 6-31G atomic orbital basis set. All results are reported in atomic units

Atom/Orbital	X	Y	Z
Nitrogen	0.0	0.0	0.0
Oxygen	0.0	0.0	2.17474
α LMO's($^2\Pi$)			
Nirrogen-1*s*	0.0	0.0	0.000493
Oxygen-1*s*	0.0	0.0	2.174295
Oxygen-1*p*1	−0.577608	0.000152	2.469459
Oxygen-1*p*2	0.577608	−0.000152	2.469459
Nirrogen-1*p*1	−0.687794	0.000180	−0.326058
Nitrogen-1*p*2	0.687794	−0.000180	−0.326058
N—O *b*1	−0.000106	−0.403531	1.094889
N—O *b*2	0.000106	0.403531	1.094889
β-LMO's($^2\Pi$)			
Nitrogen-1*s*	0.0	0.0	0.000897
Oxygen-1*s*	0.0	0.0	2.174045
Nitrogen-1*p*	0.0	0.000305	−0.639335
Oxygen-1*p*	0.000006	0.022298	2.697048
N—O *b*1	−0.405828	0.220544	1.536620
N—O *b*2	0.405944	0.220331	1.536620
N—O *b*3	−0.000122	−0.463499	1.598522
α-LMO's($^2\Sigma$)			
Nitrogen-1*s*	0.0	0.0	0.001414
Oxygen-1*s*	0.0	0.0	2.173852
Oxygen-*n*1	−0.429662	−0.421784	2.153900
Oxygen-*n*2	0.580106	−0.161206	2.153900
Oxygen-*n*3	−0.150444	0.582990	2.153900
Nitrogen-*n*1	−0.648325	0.164070	0.057255
Nitrogen-*n*2	0.466252	0.479431	0.057255
Nitrogen-*n*3	0.182073	−0.643501	0.057255
β-LMO's($^2\Sigma$)			
Nitrogen-1*s*	0.0	0.0	0.001023
Oxygen-1*s*	0.0	0.0	2.173972
Nitrogen-1*p*	0.0	0.0	−0.684408
Oxygen-1*p*	0.0	0.0	2.729738
N—O *b*1	−0.463851	0.081248	1.521221
N—O *b*2	0.302289	0.361083	1.521221
N—O *b*3	0.161562	−0.442331	1.521221

except for the orientation of the set of τ-bonds. Subsequent iterations seem to become progressively more inefficient at rotating this set of orbitals into the correct alignment.

The convergence problems inherent in the first-order methods are caused by the need to mix each pair of τ-bonds by an amount which depends on their relation to each of the C—H bonds, not on their relation to each other. The transformation given in Eq. (44), like the conventional (2×2) rotation schemes, considers only the pairwise interactions among the orbitals, and ignores the influence of a third orbital on the rotation of any pair of orbitals. Consequently, such methods not only converge very slowly, but they may yield premature apparent convergence because of their insensitivity to the conditions required to obtain convergence.

In order to overcome these difficulties, Kleier et al. [32] introduced the "eigenvector method", in which the transformation matrix, $\boldsymbol{T}$, is determined by the eigenvector of the hessian matrix associated with the eigenvalue of smallest magnitude. The second-order approach proposed in Eq. (42) performs this type of transformation simultaneously for all eigenvalues of the hessian. In the case of methylacetylene, the magnitude of the smallest eigenvalue is much smaller than any of the remaining eigenvalues, thus there is little difference between the effects of the current method and Kleier's approach.

The method proposed here, however, requires only the inversion of the hessian matrix and does not require the explicit calculation of any eigenvector or eigenvalue of $\boldsymbol{G}_2$. It is useful to calculate a small number of eigenvalues and eigenvectors at beginning and end of a second-order localization to check for zero or positive eigenvalues, but it is not necessary to calculate these quantities for every iteration.

The orbital centroids for the LMO's of methylacetylene are shown in Table 6. These results are based on a closed-shell SCF calculation using an STO-3G basis set, the experimental geometry of Herzberg [51], and the orbital centroid

Table 6. Molecular geometry and locations of orbital centroids of LMO's for methylacetylene (C_3H_4). These results are based on the orbital centroid criterion and a STO-3G atomic orbital basis set. All results are reported in atomic units

Atom/Orbital	X	Y	Z
Carbon-1	0.0	1.140190	0.0
Carbon-2	0.0	−1.140190	0.0
Carbon-3	0.0	3.897190	0.0
Hydrogen-1	0.0	−3.145230	0.0
Hydrogen-2	−1.961326	4.438292	0.0
Hydrogen-3	0.980663	4.438292	1.698558
Hydrogen-4	0.980661	4.438292	−1.698558
Carbon1-1*s*	0.0	1.140041	0.0
Carbon2-1*s*	0.0	−1.139978	0.0
Carbon3-1*s*	0.0	3.896891	0.0
C1-C2 τ1	0.346250	−0.013709	0.599723
C1-C2 τ2	0.346250	−0.013709	−0.599723
C1-C2 τ3	−0.692500	−0.013709	0.0
C1-C3	0.0	2.498181	0.0
C2-H1	0.0	−2.502388	0.0
C3-H2	−1.316232	4.272459	0.0
C3-H3	0.658116	4.272459	1.139891
C3-H4	0.658116	4.272459	−1.139890

criterion of localization. In agreement with the results of Kleier et al. [32], the C—C τ-bonds and the C—H bonds of the methyl group are in an eclipsed conformation. This is consistent with the expectation of hyperconjugation between the C—C triple bond and the methyl group, which has been previously invoked to account for the shortening of the bond linking the methyl and acetylene groups [51].

The staggered orientation of the C—C triple bond and the methyl group corresponds to a saddle-point in the localization criterion. The path from this saddle-point to the fully-localized configuration essentially consists of the rotation of the set of τ-bonds by 60° about the molecular axis. Such motion is represented by an eigenvector of the hessian matrix. The eigenvalue associated with this eigenvector is positive for the 30° starting with the saddle-point (indicating divergence to the saddle-point) and negative for the 30° from the midpoint of this path to the maximum (indicating proper convergence). The initial few iterations based on Eq. (44) essentially lead to a random point on (or near) this path. Consequently, there are roughly equal probabilities of converging to a saddle-point and converging to the maximum when Eq. (42) is utilized.

Initial calculation based on Eqs. (42) and (44) led rapidly to maximum localization (eclipsed configuration). By making a minor change in the first iteration, starting with the canonical orbitals, it was possible to obtain convergence to the saddle-point (staggered) configuration. Such convergence is indicated by the presence of one (or more) positive eigenvalues of the hessian matrix. In order to move from the saddle-point towards a maximum, it is possible to move in the direction determined by the most positive eigenvalue through a transformation such as

$$\boldsymbol{t} = \lambda \boldsymbol{v}, \tag{48}$$

where $\boldsymbol{v}$ is the eigenvector associated with the most positive eigenvector and λ is a scalar. Application of such a transformation with $\lambda = -1$ has been successful in obtaining convergence to maximum localization. For methylacetylene, four second-order iterations following the transformation determined by Eq. (48) were required to transform the orbitals from the staggered to the eclipsed conformation.

4.6. *Dinitrogen Tetroxide*

The preceding examples have demonstrated that the transformation determined by Eq. (42) is very effective at providing a rapidly convergent procedure for obtaining localized orbitals, including cases in which one or more eigenvalues of $\boldsymbol{G}_2$ are very small or zero. It is well known, however, that optimization procedures such as this which are based on Newton's method suffer from two serious problems. First, this type of procedure leads to a maximum only if all of the eigenvalues are either zero or negative, with convergence to a saddle-point occurring if any eigenvalues are positive. Consequently, it is not possible to apply this scheme until the quantities to be optimized are within some limited radius of convergence from the desired values.

In the work described here, this problem is resolved by the use of the approximate $(n \times n)$ transformation of Eq. (44). This starting procedure appears to be very effective at producing a hessian matrix whose diagonal elements are all negative. The number of positive eigenvalues which remain after all the diagonal elements are negative tends to be very small, and such situations may be treated using methods such as that presented for methylacetylene in the preceding section.

The second problem is that the hessian matrix becomes extremely large for large molecules [52]. The dimensionality of the hessian grows as $n(n-1)/2$, where n is the number of orbitals being localized. Because of this, the number of matrix elements increases as n^4, and the time required to invert or diagonalize the hessian grows as n^6. Due to the delta functions contained in the definition of the off-diagonal hessian matrix elements (Eq. (40)), the number of non-zero elements only grows as n^3, but this has little influence on the n^6 effort required

Table 7. Molecular geometry and locations of orbital centroids of the LMO's of N_2O_4. These results are based on the orbital centroid criterion and a double-zeta atomic orbital basis set. All results are reported in atomic units

Atom/Orbital	X	Y	Z
Nitrogen-1	0.0	−1.653532	0.0
Nitrogen-2	0.0	1.653532	0.0
Oxygen-1	−2.050381	−2.530377	0.0
Oxygen-2	2.050381	−2.530377	0.0
Oxygen-3	−2.050381	2.530377	0.0
Oxygen-4	2.050381	2.530377	0.0
Nitrogen1-1s	0.0	−1.653548	0.0
Nitrogen2-1s	0.0	1.653548	0.0
Oxygen1-1s	−2.050113	−2.530268	0.0
Oxygen2-1s	2.050113	−2.530268	0.0
Oxygen3-1s	−2.050113	2.530268	0.0
Oxygen4-1s	2.050113	2.530268	0.0
N1-N2	0.0	0.0	0.0
N1-O1 τ1	−1.235637	−2.174678	−0.405531
N1-O1 τ2	−1.235636	−2.174677	0.405531
N1-O2 τ1	1.235637	−2.174677	0.405531
N1-O2 τ2	1.235636	−2.174677	−0.405531
N2-O3 τ1	−1.235636	2.174678	−0.405531
N2-O3 τ2	−1.235637	2.174678	0.405531
N2-O4 τ1	1.235636	2.174678	−0.405531
N2-O4 τ2	1.235636	2.174678	0.405531
Oxygen1-1p1	−1.941846	−3.053272	0.0
Oxygen1-1p2	−2.431660	−2.091921	0.0
Oxygen2-1p1	2.431660	−2.091922	−0.000001
Oxygen2-1p2	1.941846	−3.053272	0.0
Oxygen3-1p1	−1.941846	3.053272	0.0
Oxygen3-1p2	−2.431659	2.091921	0.0
Oxygen4-1p1	2.431660	2.091921	0.0
Oxygen4-1p2	1.941846	3.053272	0.0

to invert $\boldsymbol{G}_2$. At some point, the effort required to invert $\boldsymbol{G}_2$ overwhelms all other stages of the localization process, rendering this approach impractical for large molecules.

In order to obtain a practical localization procedure which is applicable to arbitrarily large molecules, the following compromise scheme has been developed. Instead of calculating the hessian matrix for all members of a set of N orbitals, a subset of the $n = 10$ to 15 least determined orbitals may be selected based on the values of the quantities D_{ij}, defined in Eq. (24). This results in a hessian matrix with a dimensionality of 45 to 105. Within this subset, the corresponding second-order subset transformation matrix is determined according to Eq. (42). The remaining elements of the full transformation matrix are then determined by Eq. (44).

The location of the LMO centroids obtained from application of this compromise procedure to N_2O_4 are provided in Table 7. These results are based on the DZ SCF molecular orbitals of Snyder and Basch [46]. This molecular involves 46 electrons in 23 molecular orbitals, with the resulting localized orbitals indicating eight equivalent N—O τ-bonds, eight equivalent oxygen lone pairs, six inner-shell orbitals and an N—N σ-bond. For this calculation, a subset of $n = 12$ orbitals was used to construct the hessian matrix. The composition of this subset was permitted to change from iteration to interation.

Because the full hessian matrix is not used, this method is no longer quadratically convergent. This deviation results from the behavior of the orbitals not selected for inclusion into the hessian subset. These orbitals tend to be strongly determined irrespective of the other orbitals present. Consequently, as shown in Table 4, this procedure converges very rapidly, in spite of the compromise involved in the treatment of the hessian matrix.

The localized orbitals obtained for this molecule imply a total of five bonds on each nitrogen atom. The Mulliken gross atomic population for each nitrogen, however, is only 6.62, indicating that each of the eight N—O τ-bonds is polarized slightly towards the oxygen atom.

5. Conclusion

The numerical results presented in this work demonstrate that highly converged localized molceular orbitals may be determined by a small number of first-order iterations based on Eq. (44), followed by a small number of second-order iterations based on Eq. (42). Applications to carbon monoxide, boron fluoride and nitric oxide demonstrate that eigenvalues of zero in the hessian matrix may be treated by freezing the appropriate elements of the transformation matrix.

Application of this procedure to methylacetylene demonstrated that the method works well when one of the eigenvalues is very small. Calculations on methylacetylene also demonstrated a method for moving from a saddle-point to an extremum.

Calculations on the nitric oxide molecule demonstrated the application of this method to an open-shell molecule. These results show that changing the occupancy of a single pair of canonical molecular orbitals can cause a dramatic change in all of the resulting valence localized molecular orbitals.

Calculations on dinitrogen tetroxide demonstrated the application of a composite method suitable for use on large molecules for which it is impractical to calculate and invert the entire hessian matrix. In this composite method, a subset hessian matrix is determined for a small number (in this case, twleve) of least-determined orbitals. The second-order procedure is used to calculate elements of the transformation matrix mixing pairs of these orbitals. All remaining elements of the transformation matrix are determined by the first-order procedure. The set of least-determined orbitals is redetermined on each iteration. Convergence is no longer fully quadratic, but is found to be very rapid.

In principle, the methods proposed here may be applied to the energy [9, 12, 13] and density [9, 11, 17] criteria of localization, as well as to the orbital centroid criterion [10, 14, 15]. Application of the second-order method to the orbital centroid criterion is facilitated by the fact that such calculations require no new integrals over molecular orbitals not required by first order methods. In contrast, application of the second-order procedure based on the other criteria requires on the order of n^3 integrals not required to localize a set of n orbitals by a first-order procedure. Consequently, all numerical results reported in this work are based on the orbital centroid criterion. Alternative procedures more appropriate to the other criteria will be presented in a separate paper [53].

Acknolwedgments. Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research. Most of the calculations reported here were performed on a PDP-11/44 computer in the Department of Chemistry at Duke University.

Appendix: Symmetric Orthonormalization

The matrix $\boldsymbol{W}$ defined in Eq. (28) can be written as

$$\boldsymbol{W} = (\boldsymbol{I} + \boldsymbol{S})^{-1/2}, \tag{A.1}$$

where $\boldsymbol{I}$ is the unit matrix and $\boldsymbol{S}$ is the off-diagonal overlap matrix for the normalized but non-orthogonal orbitals determined by the matrix $\boldsymbol{R}$ defined by Eqs. (30)–(33). It is crucial for these calculations that the matrix $\boldsymbol{W}$ be positive definite. This is not guaranteed by conventional methods for calculating $(\boldsymbol{I}+\boldsymbol{S})^{-1/2}$ based on the use of Givens–Householder methods to diagonalize $(\boldsymbol{I}+\boldsymbol{S})$. These methods may yield a matrix $\boldsymbol{W}'$, which is related to $\boldsymbol{W}$ by an arbitrary unitary transformation, and which is not positive definite. This is of no consequence in the solution of the SCF equations for a non-orthogonal set of atomic orbitals because the resulting canonical orbitals are not affected by this arbitrary transformation. In the calculation of LMO's, however, such a transformation completely destroys the localization process. Consequently, an alternate method has been adopted. The matrix $(\boldsymbol{I}+\boldsymbol{S})^{-1/2}$ can be written as [41]

$$(\boldsymbol{I}+\boldsymbol{S})^{-1/2}=\boldsymbol{I}-(1/2)\boldsymbol{S}+(3/8)\boldsymbol{S}^2+\cdots. \tag{A.2}$$

If the elements of $\boldsymbol{S}$ are very small, this series converges rapidly. The first few iterations of a localization procedure, however, may yield overlap matrix elements with magnitudes of 0.1 or greater. In this case, the series could require many more terms to obtain satisfactory convergence. To avoid the use of additional terms in Eq. (A.2), an iterative procedure has been devised and found to be very effective.

The expansion for the matrix $(\boldsymbol{I}+\boldsymbol{S})^{-1/2}$ can be truncated after second-order in $\boldsymbol{S}$, giving

$$\boldsymbol{W}^I=\boldsymbol{I}-(1/2)\boldsymbol{S}^I+(3/8)(\boldsymbol{S}^I)^2. \tag{A.3}$$

This may be used to determine a new set of orbitals defined by

$$\phi^{(I+1)}=\boldsymbol{Q}^I\phi^I, \tag{A.4}$$

where $\boldsymbol{Q}^I=\boldsymbol{W}^I\boldsymbol{N}^I$, and $\boldsymbol{W}^I$ is determined by Eq. (A.3). The overlap matrix in Eq. (A.3) is given by

$$\boldsymbol{S}^I=\boldsymbol{N}^I\boldsymbol{S}_0^I\boldsymbol{N}^I \tag{A.5}$$

where

$$S_{0ij}^I=\langle\phi_i^I|\phi_j^I\rangle \tag{A.6}$$

and

$$N_{ij}^I=S_{0ij}^{I\ \ 1/2}\delta_{ij}. \tag{A.7}$$

This is repeated until the RMS value of $\boldsymbol{S}^I$ is sufficiently small. Fewer than five iterations are usually required to reduce the RMS value from 0.1 to less than 10^{-10}. In extreme cases, where the RMS value of $\boldsymbol{S}^I$ is greater than 0.5, the procedure can be divergent. This is likely to occur on early iterations of a localization, where the orbitals may be extensively delocalized and 45° pairwise rotations are common. This may be corrected by decreasing the magnitude of the transformation being performed. For example, the magnitude of the off-diagonal elements of the transformation matrix, $\boldsymbol{T}$, may be reduced by a scalar factor until convergence is obtained.

References

1. Fock, V.: Z. Phys. **61**, 126 (1930)
2. Hartree, D. R.: Proc. Cambridge Phil. Soc. **24**, 89 (1928)
3. Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951); Roothaan, C. C. J.: Rev. Mod. Phys. **32**, 179 (1960)
4. Pople, J. A., Nesbet, R. K.: J. Chem. Phys., **22**, 571 (1954)
5. Edmiston, C., Ruedenberg, K.: J. Chem. Phys. **43**, S97 (1965)

6. Weir, A. W.: Phys. Rev. **162**, 71 (1967)
7. Stephens, W. J., Das, G., Wahl, A. C.: J. Chem. Phys. **61**, 3686 (1974)
8. Koopmans, T.: Physica **1**, 104 (1933)
9. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
10. Boys, S. F.: Quantum theory of atoms, molecules and the solid state. Lödwin, P. (ed.), New York: Academic 1966
11. von Niessen, W.: J. Chem. Phys. **56**, 4290 (1972)
12. Lennard-Jones, J. E.: Proc. R. Soc. (London) **A198**, 1, 14 (1949)
13. Hall, G. G., Lennard-Jones, J. E.: Proc. R. Soc. (London) **A202**, 155 (1950)
14. Boys, S. F.: R. Mod. Phys. **32**, 306 (1960)
15. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 300 (1960)
16. Linnett, J. W.: J. Am. Chem. Soc. **83**, 2643 (1961)
17. von Niessen, W.: J. Chem. Phys. **55**, 1948 (1971)
18. Newton, M., Switkes, E., Lipscomb, W.: J. Chem. Phys. **53**, 2645 (1970)
19. Rothenburg, S.: J. Chem. Phys. **51**, 3389 (1969)
20. Rothenburg, S.: J. Am. Chem. Soc. **93**, 68 (1971)
21. Switkes, E., Lipscomb, W., Newton, M.: J. Am. Chem. Soc. **92**, 3847 (1970)
22. Kapuy, E., Kozmutza, C., Daudel, R., Stephens, M.: Theoret. Chim. Acta **53**, 147 (1979)
23. Levy, M.: J. Chem. Phys. **65**, 2473 (1976)
24. O'Leary, B., Duke, B. J., Eilers, J. E.: Adv. Quant. Chem. **9**, 1 (1975)
25. England, W., Gordon, M. S., Ruedenberg, K.: Topics Curr. Chem. **23**, 31 (1971)
26. Diner, S., Malrieu, J. P., Claverie, P.: Theoret. Chim. Acta (Berl.) **13**, 1 (1969); Malrieu, J. P.: J. Chem. Phys. **70**, 4405 (1979)
27. Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
28. I'Haya, Y. J., Suzuki, H., Narita, S.: J. Chem. Phys. **77**, 391 (1982)
29. Luken, W. L., Beratan, D. L.: Theoret. Chim. Acta (Berl.) (1982) **61**, 265; Luken, W. L., Culberson, J. C.: Int. J. Quant. Chem. Symp. (1982) in press
30. Hunter, J. A.: Chem. Phys. Letters **68**, 199 (1979)
31. Taylor, W. J.: J. Chem. Phys. **48**, 2385 (1968)
32. Kleier, D. A., Halgren, T. A., Hall, J. H., Lipscomb, W.: J. Chem. Phys. **61**, 3905 (1974)
33. Kari, R.: Progress in theoretical organic chemistry. Csizmadia, I. G. (ed.), Vol. 2, Amsterdam: Elsevier 1977
34. Ryback, W., Poirer, R., Kari, R., Int. J. Quant. Chem. **13**, 1 (1978)
35. Adams, W. H.: J. Chem. Phys. **37**, 2009 (1962)
36. Gilbert, T. L.: Molecular orbitals in chemistry, physics, and biology, Löwdin, P. O., Pullman, B. (eds.). New York: Academic 1964
37. Ruedenberg, K.: Modern quantum chemistry, Vol. 1, Edited by Sinanoğlu, O.: New York: Academic 1965
38. Hunt, W. J., Hay, P. J., Goddard, W. A.: J. Chem. Phys. **57**, 738 (1972)
39. Bobrowicz, F. W., Goddard, W. A.: Methods of electronic structure theory. Schaefer, H. F. (ed.). New York: Plenum 1977
40. Chipman, D. M., Kirtman, B., Palke, W. E.: J. Chem. Phys. **65**, 2556 (1976)
41. Löwdin, P.: J. Chem. Phys. **18**, 365 (1950)
42. Raffenetti, R. C., Ruedenberg, K.: Int. J. Quant. Chem. **IIIS**, 625 (1970); Hoffman, D. K., Raffenetti, R. D., Ruedenberg, K.: J. Math. Phys. **13**, 528 (1972)
43. Dunning, T. H.: J. Chem. Phys. **53**, 2823 (1970); Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
44. Laidig, W. D., Saxe, P., Schaefer, H. F.: J. Chem. Phys. **73**, 1765 (1980); Saxe, P., Schaefer, H. F., Handy, N. C.: Chem. Phys. Letters **79**, 202 (1981)
45. von Niessen, W.: Theoret. Chim. Acta (Berl.) **29**, 29 (1973)
46. Snyder, L. C., Basch, H.: Molecular wavefunctions and properties, New York: Wiley-Interscience 1972
47. England, W.: Int. J. Quant. Chem. **5**, 683 (1971)
48. Kurtz, H. A., Jordan, K. D.: Chem. Phys. Letters **81**, 104 (1981)
49. Hehre, W. J., Ditchfield, R., Pople, J. A.: J. Chem. Phys. **56**, 2256 (1972)
50. Hirst, D. M., Linington, M. E.: Theoret. Chim. Acta (Berl.) **16**, 55 (1970)

51. Herzberg, G.: Molecular spectra and molecular structure III. Electronic spectra and electronic structure of polyatomic molecules, New York: Van Nostrand Reinhold 1966
52. Pulay, P.: Chem. Phys. Letters **73**, 393 (1980)
53. Leonard, J., Luken, W. L.: in preparation

Received May 14/July 28, 1982