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Localized orbitals based on the Fermi hole

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The Fermi hole provides a direct (non-iterative) method for tansforming canonical SCF molecular orbitals into localized orbitals. Except for simple overlap integrals required to maintain orthogonality, this method requires no integrals over orbitals or basis functions. This method is demonstrated by application to a furanone ($C_4H_4O_2$), methylacetylene, and boron trifluoride. The results of these calculations are compared to those determined by the orbital centroid criterion of localization.

Key words: Molecular orbitals—localized orbitals—Fermi hole—density matrix

1. Transformations of SCF orbitals

The observable properties of any wavefunction composed of a single Slater determinant are invariant to a unitary transformation of the orbitals occupied in the wavefunction [1]. Because of this invariance, the observable properties of a closed-shell self-consistent field (SCF) wavefunction may be described using canonical SCF orbitals, localized SCF orbitals [2–9], or any other orbitals related to the canonical SCF orbitals by a unitary transformation.

This paper presents a method for transforming a set of canonical SCF orbitals into a set of localized orbitals based on the properties of the Fermi hole [10–14] and the Fermi orbital [15, 16]. Unlike localization methods based on iterative optimization of some criterion of localization [3–9], the method presented here provides a direct (non-iterative) calculation of the localized orbital transformation matrix. Consequently, this method avoids the convergence problems which are possible with iterative transformations.

Unlike the extrinsic methods for transforming canonical SCF orbitals into localized orbitals [17-19], the method presented here does not depend on the introduction or definition of a set of "atomic orbitals". The method presented here may also be distinguished from applications of localized orbitals such as the PCILO method [20-25] in that the latter method does not involve SCF orbitals, and it is not concerned with the transformation of canonical SCF orbitals into localized orbitals.

2. Properties of the Fermi hole

The Fermi hole is defined as

$$\Delta(\boldsymbol{r}_1;\boldsymbol{r}_2)=\rho(\boldsymbol{r}_1)-2\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)/\rho(\boldsymbol{r}_2), \tag{1}$$

where $\rho(\boldsymbol{r}_1)$ is the diagonal portion of the first order reduced density matrix and $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the corresponding part of the second order reduced density matrix [26]. For the special case of a closed shell SCF wavefunction, the natural representation of the Fermi hole is the absolute square of the Fermi orbital [15, 16]

$$\Delta(\boldsymbol{r}_1;\boldsymbol{r}_2)=|f(\boldsymbol{r}_1;\boldsymbol{r}_2)|^2. \tag{2}$$

The Fermi orbital is given by

$$f(\boldsymbol{r}_1;\boldsymbol{r}_2)=[2/\rho(\boldsymbol{r}_2)]^{1/2}\sum_i g_i(\boldsymbol{r}_1)g_i(\boldsymbol{r}_2), \tag{3}$$

where the orbitals $g_i(\boldsymbol{r})$ are either the canonical SCF moecular orbitals or any set related to the canonical SCF molecular orbitals by a unitary transformation. The Fermi orbital $f(\boldsymbol{r}_1;\boldsymbol{r}_2)$ is interpreted as a function of $\boldsymbol{r}_1$ which is parametrically dependent upon the position of a probe electron located at $\boldsymbol{r}_2$.

Previous work in this laboratory [15, 27-29] has demonstrated that the Fermi hole does not follow the probe electron in a uniform manner. Instead, molecules are found to possess regions where the Fermi hole is insensitive to the position of the probe electron. As the probe electron passes through one of these regions, the Fermi hole remains nearly stationary with respect to the nuclei. These regions are separated by regions where the Fermi hole is very sensitive to the position of the probe electron. As the probe electron passes through one of these regions, the Fermi hole changes rapidly from one stable form to another.

The sensitivity of the Fermi hole to the position of the probe electron is measured by the Fermi hole mobility function [27-29],

$$F(\boldsymbol{r})=F_x(\boldsymbol{r})+F_y(\boldsymbol{r})+F_z(\boldsymbol{r}) \tag{4}$$

where

$$F_v(\boldsymbol{r})=\frac{2}{\rho^2}\sum_{i>j}\left[g_i\left(\frac{\partial g_j}{\partial v}\right)-g_j\left(\frac{\partial g_i}{\partial_v}\right)\right]^2, \tag{5}$$

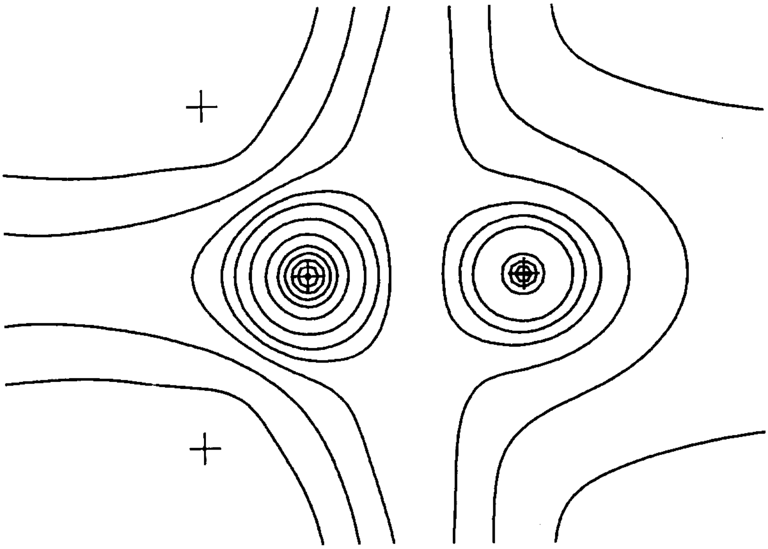

Fig. 1. The Fermi hole mobility function $F(r)$ for the formaldehyde molecule H_2CO based on the geometry and double zeta basis set of Ref. [41]. The locations of the nuclei are indicated by (+) signs. The contours represent mobility function values of 0.1, 0.25, 0.5, 1.0, 2.0, 5.0 atomic units. The contours increase from 0.1 near the corners, to over 5.0 in regions enclosing the carbon and oxygen nuclei. Each nucleus is located at local minimum of the mobility function

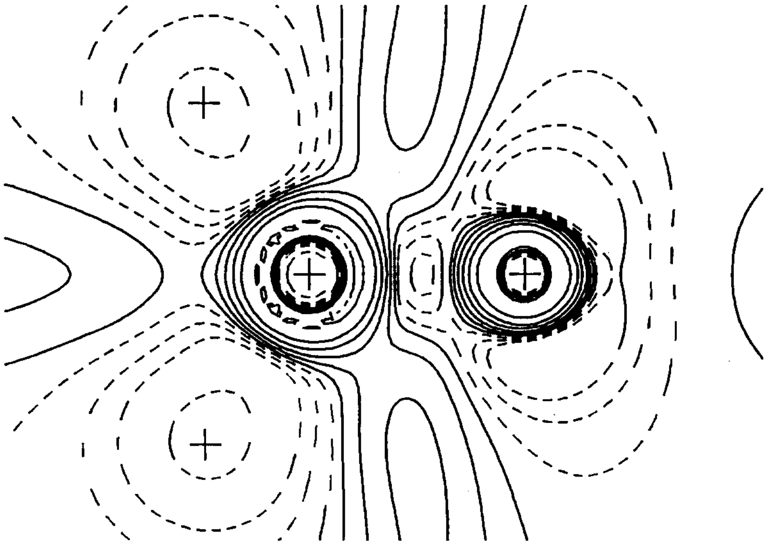

Fig. 2. The difference between the Fermi hole mobility function $F(r)$ and the electron gas approximation $F_0(\rho)$ for the formaldehyde molecule. The contours represent values of 0.0, −0.1, −0.25, −0.5, −1.0, −2.0, and −5.0, in addition to those indicated in Fig. 1. The contours representing negative values and zero are indicated by broken lines. Each nucleus is located at a local minimum

for $v = x$, y, and z. This may be compared to

$$F_0(\rho) = (3\pi/4)(\rho/2)^{2/3} \tag{6}$$

which provides an estimate of the Fermi hole in a uniform density electron gas.

The Fermi hole mobility function $F(\boldsymbol{r})$ for the formaldehyde molecule is shown in Fig. 1. The difference $F(\boldsymbol{r}) - F_0(\rho)$ is shown in Fig. 2. Regions where $F(\boldsymbol{r}) > F_0(\rho)$, that is, the Fermi hole is less sensitive to the position of the probe electron than it would be in an electron gas of the same density, may be compared to the loges proposed by Daudel [30-33]. Regions where $F(\boldsymbol{r}) > F_0(\rho)$ resemble the boundaries between loges.

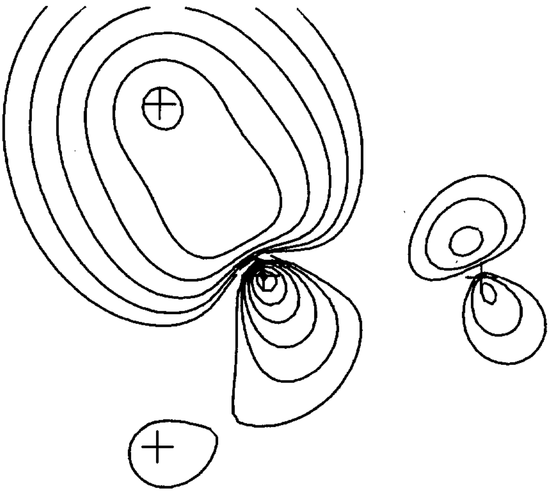

Fig. 3. The Fermi hole for the formaldehyde molecule determined by a probe electron located at one of the protons. The contours indicate electronic density values of 0.005, 0.01, 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, 1.28, and 2.56 electrons per cubic bohr

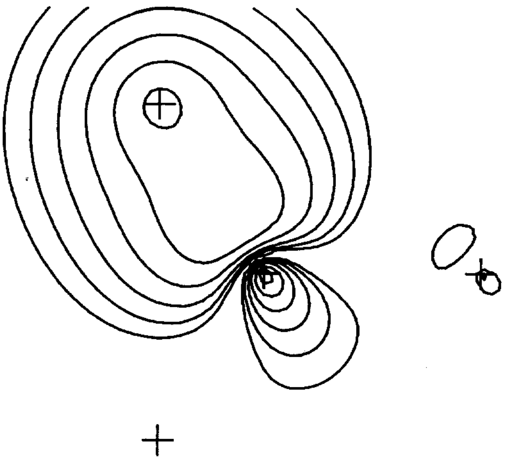

Fig. 4. The localized orbital for the C-H bond of a formaldehyde molecule determined by the orbital centroid criterion of localization. The electronic density contours are the same as in Fig. 3

When the probe electron is located in a region where $F(\boldsymbol{r}) < F_0(\rho)$, the Fermi orbital is found to resemble a localized orbital determined by conventional methods [3-9]. This similarity is demonstrated by Figs. 3 and 4 which compare a Fermi hole for the formaldehyde molecule with a localized orbital determined by the orbital centroid criterion of localization [5-8].

3. Localized orbitals based on the Fermi hole

Eq. 3 provides a direct relationship between a set of canonical SCF orbitals $g_i(\boldsymbol{r})$ and a localized orbital $f_j(\boldsymbol{r}) = f(\boldsymbol{r}; \boldsymbol{r}_j)$, where $\boldsymbol{r}_j$ is a point in a region where $F(\boldsymbol{r}_j) < F_0(\rho(\boldsymbol{r}_j))$. In order to transform a set of N canonical SCF orbitals into a set of N localized orbitals, it is necessary to select N points $\boldsymbol{r}_j$, $j = 1$ to N, each of which is located in a region where $F(\boldsymbol{r}_j) < F_0(\rho(\boldsymbol{r}_j))$. Ideally, each of these points should correspond to a minimum of $F(\boldsymbol{r})$ or $F(\boldsymbol{r}) - F_0(\rho)$. This condition, however, is not critical, because the Fermi hole is relatively insensitive to the position of the probe electron when the probe electron is located in one of these regions.

A set of N Fermi orbitals determined by Eq. 3 is not generally orthonormal. Each member of this set, however, is usually very similar to one member of an orthonormal set of conventional localized orbitals. Consequently, the overlap between a pair of Fermi orbitals is usually very small, and a set of N Fermi orbitals may easily be converted into an orthonormal set of localized orbitals by means of the method of symmetric orthogonalization [34]. The resulting unitary transformation is given by

$$\boldsymbol{U} = (\boldsymbol{T}\boldsymbol{T}^{\dagger})^{-1/2}\boldsymbol{T}, \tag{7}$$

where

$$T_{ij} = g_j(\boldsymbol{r}_i)/(\rho(\boldsymbol{r}_i)/2)^{1/2}. \tag{8}$$

In the following three sections, the transformation of canonical SCF orbitals to localized orbitals based on Eqs. 7 and 8 is demonstrated for each of three molecules. The first example, a cyclic conjugated enone, represents a simple case where conventional methods are not expected to have any special difficulties. The second example, methyl acetylene, is a molecule for which conventional methods have serious convergence problems [35]. The third example, boron trifluoride, is a pathological case for the orbital centroid criterion, with a number of local maxima and saddle points in the criterion of localization.

In each case, the first step in the application of this method is the selection of the set of N points. This set always includes the locations of all of the nuclei in the molecule. For atoms other than hydrogen, the resulting Fermi orbitals are similar to innershell localized orbitals. When the probe electron is located on a hydrogen atom, the Fermi orbital is similar to an R-H bond orbital.

Additional points for the probe electron may usually be determined based on the molecular geometry. The midpoint between two bonded atoms (other than hydrogen) tends to yield a Fermi orbital resembling a single bond. Multiple bonds may be represented with two or three points located roughly one to two bohr from a point midway between the multiply bonded atoms, along lines perpendicular to a line joining the nuclei. Likewise, lone pair orbitals may be determined by points located roughly one bohr from the nucleus of an atom which is expected to possess lone pair orbitals.

4. Application to the furanone molecule

The furanone molecule, $C_4H_4O_2$, and its derivatives, are useful reagents in 2+2 photochemical cycloadditions [36-38]. The canonical SCF molecular orbitals for the furanone molecule were calculated with an STO-3G [39] basis set and the geometry specified in Table 1. The molecular geometry was restricted to C_s symmetry, with a planar five membered ring. Fermi hole localized orbitals were calculated based on the set of points indicated in Table 1. These points include the positions of the ten nuclei, as well as twelve additional points determined by the method outlined above.

Table 1. Molecular geometry and probe electron points for the furanone ($C_4H_4O_2$). The first ten points indicate the molecular geometry used in these calculations. The twelve additional probe electron positions were determined as described in the text. All coordinates are given in bohr

position	X	Y	Z
atom C-1	0.0	0.0	0.0
atom C-2	0.0	2.589	0.0
atom C-3	2.671	3.355	0.0
atom C-4	4.363	0.940	0.0
atom 0-1	2.534	−1.071	0.0
atom 0-2	3.427	5.548	0.0
atom H-1	−1.802	−1.040	0.0
atom H-2	−1.802	3.629	0.0
atom H-3	5.560	0.858	1.698
atom H-4	5.560	0.858	−1.698
C-1, C-2 bond-1	0.0	1.295	2.000
C-1, C-2 bond-2	0.0	1.295	−2.000
C-2, C-3 bond	1.336	2.972	0.0
C-3, C-4 bond	3.517	2.148	0.0
C-4, 0-1 bond	3.449	−0.066	0.0
C-1, 0-1 bond	1.267	−0.536	0.0
C-3, 0-2 bond-1	3.049	4.452	2.000
C-3, 0-2 bond-2	3.049	4.452	−2.000
0-1 lone pair-1	2.654	−1.821	0.660
0-1 lone pair-2	2.654	−1.821	−0.660
0-2 lone pair-1	2.707	6.298	0.0
0-2 lone pair-2	4.267	5.698	0.0

Table 2. Orbital centroids for localized orbitals determined by the Fermi hole method and by the orbital centroid method for the furanone molecule ($C_4H_4O_2$). All coordinates are given in bohr

	Fermi hole method			Centroid criterion		
Orbital	*X*	*Y*	*Z*	*X*	*Y*	*Z*
C-1 *K* shell	0.0003	0.0011	0.0	0.0001	0.0	0.0
C-2 *K* shell	0.0009	2.5881	0.0	0.0001	2.5887	0.0
C-3 *K* shell	2.6708	3.3553	0.0	2.6710	3.3550	0.0
C-4 *K* shell	4.3626	0.9401	0.0	4.3269	0.9399	0.0
0-1 *K* shell	2.5340	−1.0703	0.0	2.5339	−1.0703	0.0
0-2 *K* shell	3.4273	5.5479	0.0	3.4268	5.5474	0.0
C-1, H-1 bond	−1.1382	−0.7426	0.0	−1.1719	−0.7614	0.0
C-2, H-2 bond	−1.1487	3.3183	0.0	−1.1817	3.3312	0.0
C-4, H-3 bond	5.1490	0.8951	1.1325	5.1559	0.8889	1.1537
C-4, H-4 bond	5.1490	0.8951	−1.1325	5.1559	0.8889	−1.1537
C-1, C-2 bond-1	0.0082	1.4019	0.6357	0.0300	1.4107	0.5998
C-1, C-2 bond-2	0.0082	1.4019	−0.6357	0.0300	1.4107	−0.5998
C-2, C-3 bond	1.3202	3.0542	0.0	1.2847	3.0467	0.0
C-3, C-4 bond	3.5422	2.1909	0.0	3.5654	2.1496	0.0
C-4, 0-1 bond	3.2682	−0.2437	0.0	3.2433	−0.2252	0.0
C-1, 0-1 bond	1.4724	−0.6277	0.0	1.4953	−0.6136	0.0
C-3, 0-2 bond-1	3.0936	4.5846	0.5480	3.1143	4.6127	0.5112
C-3, 0-2 bond-2	3.0936	4.5846	−0.5480	3.1143	4.6127	−0.5112
0-1 lone pair-1	2.5548	−1.2836	0.4407	2.5942	−1.3110	0.4724
0-1 lone pair-2	2.5548	−1.2836	−0.4407	2.5942	−1.3110	−0.4724
0-2 lone pair-1	3.0157	5.8864	0.0	3.0111	5.8920	0.0
0-2 lone pair-2	3.9706	5.5890	0.0	3.9702	5.6005	0.0

The centroids of the localized orbitals determined by the points in Table 1 are shown in Table 2. The C=C and C=O double bonds are each represented by a pair of equivalent bent (banana) bonds similar to those determined by other methods for transforming canonical SCF orbitals into localized orbitals.

As shown in Table 2, the centroids of the orbitals determined by the Fermi hole are very close to those of the localized orbitals determined by the orbital centroid criterion [5–8]. Likewise, the localized orbitals determined by the Fermi hole were found to be very close to those determined by the orbital centroid criterion. Each of the localized orbitals determined by the Fermi hole method was found to have an overlap of 0.994 to 0.999 with one of the localized orbitals determined by the orbital centroid criterion. The remaining (off-diagonal) overlap integrals between these two sets of localized orbitals were found to have a root mean square (RMS) value of 0.011734.

The transformation of a set of canonical SCF orbitals to an orthonormal set of localized orbitals determined by the Fermi hole required 10 minutes on a PDP-11/44 computer. The orbital centroid criterion method required 140 minutes starting from the canonical SCF molecular orbitals or 80 minutes, using the Fermi localized orbitals as an initial guess, to reach T_{RMS} of less than 10^{-5}, where T_{RMS}

is the RMS value of the off-diagonal part of the transformation matrix which converts the orbitals obtained on one iteration to those of the next iteration. The orbital centroid criterion calculations reported here are based on a partially quadratic procedure [8] which requires less time than conventional localization procedures based on 2 × 2 rotations.

5. Application to methylacetylene

The localized orbitals of methylacetylene are of interest because of the convergence difficulties encountered in attempts to calculate these orbitals using iterative localization methods. These difficulties are caused by the weak dependence of the criterion of localization on the orientation of the three equivalent C–C (banana) bonds relative to the three C–H bonds of the methyl group. In calculations based on the orbital centroid criterion, over 200 iterations were required to determine a set of orbitals which satisfied a very weak criterion of convergence [35]. Most of these difficulties may be overcome using the quadratically convergent method which has been developed recently [8]. As shown below, however, the localized orbitals based on the Fermi hole yield nearly equivalent results and require much less effort than even the quadratically convergent method.

The canonical SCF molecular orbitals for methylacetylene were determined by an STO-5G basis set [39] and an experimental geometry [40]. Transformation of the 11 occupied SCF orbitals into localized orbitals based on the Fermi hole method required the selection of 11 points. These points are shown in Table 3. The positions of the nuclei provided 7 of these points. One point was located at the midpoint of the C_2–C_3 single bond. The remaining three points were located 2 bohr from the C_3 rotation axis, in a plane perpendicular to the C_3 rotation axis. This plane intersects the C_3 rotation axis at a point midway between the C_1 and C_2 nuclei. These last three points were eclipsed with respect to the methyl protons.

Table 3. Molecular geometry and probe electron positions for the methylacetylene molecule. The first seven points indicate the locations of the nuclei. All coordinates are given in bohr

position	*X*	*Y*	*Z*
atom C-1	0.0	−1.1402	0.0
atom C-2	0.0	1.1402	0.0
atom C-3	0.0	3.8972	0.0
atom H-1	0.0	−3.1452	0.0
atom H-2	−1.9613	4.4383	0.0
atom H-3	0.9807	4.4383	1.6986
atom H-4	0.9807	4.4383	−1.6986
C-1, C-2 bond-1	−2.0	0.0	0.0
C-1, C-2 bond-2	1.0	0.0	1.7321
C-1, C-2 bond-3	1.0	0.0	−1.7321
C-2, C-3 bond	0.0	2.5100	0.0

Table 4. Orbital centroids for localized orbitals determined by the Fermi hole method and by the orbital centroid method for the methylacetylene molecule. All coordinates are given in bohr

	Fermi hole method			Centroid criterion		
Orbital	*X*	*Y*	*Z*	*X*	*Y*	*Z*
C-1 *K* shell	0.0	−1.1410	0.0	0.0	−1.1400	0.0
C-2 *K* shell	0.0	1.1396	0.0	0.0	1.1340	0.0
C-3 *K* shell	0.0	3.8964	0.0	0.0	3.8969	0.0
C-1, H-1 bond	0.0	−2.4860	0.0	0.0	−2.5024	0.0
C-3, H-2 bond	−1.3022	4.2704	0.0	−1.3162	4.2725	0.0
C-3, H-3 bond	0.6511	4.2704	1.1277	0.6581	4.2725	1.1399
C-3, H-4 bond	0.6511	4.2704	−1.1277	0.6581	4.2725	−1.1399
C-1, C-2 bond-1	−0.7131	−0.0039	0.0	−0.6925	−0.0137	0.0
C-1, C-2 bond-2	0.3565	−0.0039	0.6175	0.3463	−0.0137	0.5997
C-1, C-2 bond-3	0.3565	−0.0039	−0.6175	0.3463	−0.0137	−0.5997
C-2, C-3 bond	0.0	2.4577	0.0	0.0	2.4982	0.0

The centroids of the localized orbitals determined by this method are shown in Table 4. As expected, the triple bond is represented with three equivalent banana bonds. The centroids of the corresponding orbitals determined by the orbital centroid criterion are also shown in Table 4. These are very close to those determined by the Fermi hole method. The RMS value of the off-diagonal part of the overlap matrix between the localized orbitals determined by the Fermi hole and those determined by the orbital centroid criterion is 0.012874.

The Fermi hole method required 1.62 minutes to transform the canonical SCF molecular orbitals into an orthonormal set of localized molecular orbitals. By comparison, the (quadratically convergent) orbital centroid method required 26 minutes starting from the canonical SCF molecular orbitals or 19 minutes using the Fermi localized orbitals as an initial guess to reach T_{RMS} of 10^{-8} or less.

6. Application to boron trifluoride

As a further example of the application of the Fermi hole localization method, localized orbitals were also calculated for the boron trifluoride molecule. This molecule provides a demonstration of how characteristics of little or no physical significance can cause serious convergence difficulties for iterative localization methods. A localized representation of boron trifluoride includes four inner-shell orbitals, three boron fluorine bond orbitals, and nine fluorine lone pair orbitals. The orbital centroid criterion method shows a small dependence on rotation of each set of three lone pair orbitals about the corresponding B–F axis. Consequently, the hessian matrix for the criterion of localization as a function of a unitary transformation of the orbitals has three very small eigenvalues.

The optimal orientation of the fluorine lone pairs may correspond to one of several possible conformations. One of these, the "pinwheel" conformation, has a single lone pair orbital on one of the fluorine atoms in the plane of the molecule. The other two lone pair orbitals on this fluorine atom are related to the first lone pair by 120 degree rotations about the F–B axis. The lone pair orbitals on the other two fluorines are obtained by 120 degree rotations about the C_3 axis. The point group of the orbital centroids for this conformation is C_{3h}.

The "three-up" conformation is generated by rotating the set of lone pair orbitals on each fluorine atom in the pinwheel conformation by 90 degrees about each F–B axis. The point group for the orbital centroids of this conformation is C_{3v}. The "up-up-down" conformation is generated by rotating the set of lone pair orbitals on one of the fluorine atoms in the "three-up" conformation by 180 degrees about the F–B axis. This conformation has the symmetry of the C_s point group.

The canonical SCF orbitals for BF_3 were calculated based on the double-zeta basis set and geometry tabulated by Snyder and Basch [41]. Localized orbitals determined by the orbital centroid criterion were obtained for the three-up conformation and the up-up-down conformation. The centroids for these orbitals are shown in Table 5. The first five (most positive) eigenvalues of the hessian matrix for each of these conformations are shown in Table 6. All eigenvalues of the hessian matrix are negative for both of these conformations, indicating that both conformations are maxima for the sum of squares of the orbital centroids. The pinwheel conformation, however, was never found. Consequently, it was not possible to exclude the possibility that the pinwheel conformation was the global maximum and the three-up conformation was only a local maximum.

The pinwheel conformation can easily be constructed using the Fermi hole localization method by selecting an appropriate set of probe positions. This set

Table 5. Orbital centroids for localized orbitals determined by the orbital centroid method for the boron trifluoride molecule. The four innershell orbitals have been excluded from these calculations. All coordinates are given in bohr

	up-up-up (C_{3v})			up-up-down (C_s)		
Orbital	*X*	*Y*	*Z*	*X*	*Y*	*Z*
B, F-1 bond	1.7258	0.0	−0.0722	1.7256	−0.0001	−0.0707
B, F-2 bond	−0.8629	1.4946	−0.0722	−0.8629	1.4943	−0.0707
B, F-3 bond	−0.8629	−1.4946	−0.0722	−0.8627	−1.4942	0.0692
F-1 lone pair 1	2.4451	0.0	0.4874	2.4463	0.0007	0.4871
lone pair 2	2.5968	0.4337	−0.2076	2.5963	0.4334	−0.2086
lone pair 3	2.5968	−0.4337	−0.2076	2.5963	−0.4339	−0.2075
F-2 lone pair 1	−1.2226	2.1175	0.4874	−1.2226	2.1188	0.4871
lone pair 2	−0.9228	2.4657	−0.2076	−0.9228	2.4651	−0.2086
lone pair 3	−1.6740	2.0320	−0.2076	−1.6740	2.0315	−0.2075
F-3 lone pair 1	−1.2226	−2.1175	0.4874	−1.2237	−2.1196	−0.4869
lone pair 2	−0.9228	−2.4657	−0.2076	−0.9224	−2.4648	0.2086
lone pair 3	−1.6740	−2.0320	−0.2076	−1.6734	−2.0312	0.2086

Table 6. Values of the orbital centroid criterion and the second derivatives of the orbital centroid criterion for various conformations of localized orbitals for the boron trifluoride molecule. The row labelled sum indicates the sum of squares of the orbital centroids for each of the indicated conformations. The following rows indicate the five highest (most positive) eigenvalues λ_i of the corresponding hessian matrix. The first and second column correspond to the localized orbitals described in Table 5. The third and fourth columns refer to the localized orbitals described in Table 8. The gradient vectors are zero for the first three columns

	up-up-up	up-up-down	pinwheel	Fermi hole
sum	69.445 360	69.444 985	69.438 724	69.341 094
λ_1	−0.019 521	−0.018 174	+0.017 234	+0.031 444
λ_2	−0.019 850	−0.018 914	+0.016 238	+0.029 932
λ_2	−0.019 850	−0.019 095	+0.016 236	+0.029 928
λ_4	−0.155 480	−0.153 827	−0.193 521	−0.195 502
λ_5	−0.155 484	−0.155 181	−0.194 366	−0.195 524

of points is shown in Table 7. The centroids of the resulting set of localized orbitals are shown in Table 8. When this set of localized orbitals is used as the starting point, the orbital centroid method quickly converges to a stationary point with C_{3h} symmetry. The centroids of the resulting set of orbitals are shown in Table 8. As shown in Table 6, three of the eigenvalues of the hessian matrix were positive at this point, demonstrating that the pinwheel conformation is a saddle point with respect to the orbital centroid criterion. These calculations also indicate that the three-up conformation is probably the global maximum for the orbital centroid criterion.

Table 7. Probe electron positions for the boron trifluoride molecule. The first three points are located at the midpoint of the B–F bonds. The remaining points have been chosen in the pinwheel conformation (symmetry C_{3h}). All coordinates are given in bohr

position	X	Y	Z
B, F-1 bond	1.2236	0.0	0.0
B, F-2 bond	−0.6118	1.0597	0.0
B, F-3 bond	−0.6118	−1.0597	0.0
F-1 lone pair 1	2.7812	0.9430	0.0
lone pair 2	2.7182	−0.4720	0.8170
lone pair 3	2.7812	−0.4720	−0.8170
F-2 lone pair 1	−2.2076	1.9374	0.0
lone pair 2	−0.9816	2.6444	0.8170
lone pair 3	−0.9816	2.6444	−0.8170
F-3 lone pair 1	−0.5736	−2.8804	0.0
lone pair 2	−1.7996	−2.1724	0.8170
lone pair 3	−1.7996	−2.1724	−0.8170

Table 8. Orbital centroids for localized orbitals determined by the Fermi hole method and by the orbital centroid method for the boron trifluoride molecule. The four innershell orbitals have been excluded from these calculations. All coordinates are given in bohr

	Fermi hole			Centroid criterion		
Orbital	X	Y	Z	X	Y	Z
B, F-1 bond	1.7137	0.0001	0.0	1.7203	0.0286	0.0
B, F-2 bond	−0.8570	1.4840	0.0	−0.8849	1.4755	0.0
B, F-3 bond	−0.8570	−1.4840	0.0	−0.8354	1.5041	0.0
F-1 lone pair 1	2.5675	0.4880	0.0	2.6037	0.4849	0.0
lone pair 2	2.5382	−0.2440	0.4140	2.5202	−0.2568	0.4103
lone pair 3	2.5382	−0.2440	−0.4140	2.5202	−0.2568	−0.4103
F-2 lone pair 1	−1.7064	1.9767	0.0	−1.7218	2.0125	0.0
lone pair 2	−1.0577	2.3201	0.4140	−1.0377	2.3109	0.4103
lone pair 3	−1.0577	2.3201	−0.4140	−1.0377	2.3109	−0.4103
F-3 lone pair 1	−0.8612	−2.4676	0.0	−0.8820	−2.4973	0.0
lone pair 2	−1.4804	−2.0761	0.4140	−1.4825	−2.0542	0.4103
lone pair 3	−1.4804	−2.0761	−0.4140	−1.4825	−2.0542	−0.4103

We do not intend to attribute any special physical significance to any of the lone pair configurations for BF_3. These calculations demonstrate some of the problems, such as local maxima and saddle points, which may occur for conventional iterative localization methods. These calculations demonstrate how the Fermi hole method may be used by itself to transform the canonical SCF orbitals into localized orbitals without any of these difficulties. In addition, these calculations demonstrate how the Fermi hole method may be used in conjunction with the orbital centroid method to establish a characteristic of the orbital centroid criterion which would have been very difficult to establish using the orbital centroid method alone.

7. Conclusions

The numerical results presented here demonstrate how the properties of the Fermi hole may be used to transform canonical SCF molecular orbitals into a set of localized SCF molecular orbitals. Except for the symmetric orthogonalization, this method requires no integrals and no iterative transformations. The localized orbitals obtained from this method are very similar to the localized orbitals determined by the orbital centroid criterion. The orbitals determined by the Fermi hole may be used directly in subsequent calculations requiring localized orbitals. Alternatively, the orbitals determined by this method may be used as a starting point for iterative localization procedures [3–9].

The necessity of providing the set of probe electron positions may appear to introduce a subjective element into the localized orbitals determined by the Fermi hole method. Most of the subjective character to this choice, however, is eliminated by the fact that Fermi hole is relatively insensitive to the location of the probe electron whenever the probe electron is located in a region associated with a strongly localized orbital. This is reflected by the fact that the centroids of the localized orbitals determined by the Fermi hole method, as shown in Tables 2, 4 and 8, are much closer to the centroids of the corresponding localized orbitals determined by the orbital centroid criterion than they are to the probe electron positions used to calculate them.

If the electrons are not strongly localized in certain portions of a molecule, such as in the lone pairs of a fluorine atom, then the Fermi hole may be more strongly dependent on the location of the probe electron than where the electrons are strongly localized. In such cases, the localized orbitals determined by the Fermi hole method may reflect the locations of the probe electron points more strongly than they are reflected in well localized regions. In such regions, however, there may be no physically meaningful way to distinguish between the localized orbitals determined by this method and those determined by any other method. In these situations, the Fermi hole method may provide a practical method for avoiding the convergence problems which may be expected for iterative methods when the electrons are not well localized.

The electronic structure of most common stable molecules may be described by an obvious set of chemical bonds, lone pair orbitals, and innershell atomic orbitals. This is reflected in the success of methods such as molecular mechanics [42, 43] for predicting the geometries of complex molecules. The localized orbitals of such molecules are unlikely to be the objects of much interest in themselves, but they may be useful in the calculation of other properties of a molecule, such as the correlation energy [44], spectroscopic constants [45, 46], and other properties [47, 48]. The selection of a set of probe electron positions for one of these molecules is simple and unambiguous, and the method presented here has significant practical advantages compared to alternative methods for transforming canonical SCF molecular orbitals into localized molecular orbitals.

For some molecules, the pattern of bonding may not be unique or it may not be entirely obvious, even when the geometry is known. For example, two or more alternative (resonance) structures may be involved in the electronic structure of such molecules. The localized orbitals of such molecules may be of interest in themselves, in order to characterize the electronic structure of such molecules, in addition to their utility in subsequent calculations [44–48]. In order to apply the current method to such molecules, the Fermi hole mobility function [28, 29] must be used to resolve any ambiguities which may arise in the selection of the probe electron positions. If two or more bonding schemes are possible, the positions of the probe electrons should be chosen to provide the minimum values of the Fermi hole mobility functions $F(r)$ or the mobility function difference $F(\boldsymbol{r})-F_0(\rho)$.

In the case of methylacetylene, for example, the C–C single bond may be determined by a single point midway between the carbon atoms, where $F(\boldsymbol{r})$ is less than $F_0(\rho)$. Any attempt to represent this portion of the molecule with a double bond would require placing a probe electron away from the C–C axis, in a region where $F(\boldsymbol{r})$ is greater than $F_0(\rho)$. Consequently, it is not possible to represent methylacetylene with a structure like H-C=C=CH_3 without placing one or more probe electron points in regions where the Fermi hole is unstable.

In extreme cases, even the Fermi hole mobility function may fail to provide unambiguous positions for the probe electrons. This is expected in highly conjugated aromatic molecules, metallic conductors, and other highly delocalized systems. For these electrons, the method presented here, as well as all other methods for calculating localized orbitals, are entirely arbitrary. The electronic structure of such a delocalized system may be represented by an unlimited number of localized descriptions, each of which is equally valid.

If there is a need for imposing a localized description on a highly delocalized system, the current method would be no less arbitrary than existing alternatives. The arbitrariness of the current method would be manifested in the choice of the probe electron positions for the delocalized electrons. However, the current method would continue to provide practical advantages over alternative transformations. These advantages include the absence of integrals to evaluate, the absence of iteratively repeated calculations, and the absence of convergence problems.

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References

1. Fock, V.: Z. Physik **61**, 126 (1930)
2. Lennard-Jones, J. E., Pople, J. A.: Proc. Roy. Soc. (London) **A202**, 155 (1950)
3. Edmiston, C., Ruedenberg, K.: Rev. Mod. Phys. **35**, 457 (1963)
4. Edmiston, C., Ruedenberg, K.: J. Chem. Phys. **43**, S97 (1965)
5. Boys, S. F.: in Quantum Theory of Atoms, Molecules and the Solid State, p. 253, Löwdin P., Ed., New York: Academic 1966
6. Boys, S. F.: Rev. Mod. Phys. **32**, 306 (1960)
7. Foster, J. M., Boys, S. F.: Rev. Mod. Phys. **32**, 300 (1960)
8. Leonard, J. M., Luken, W. L.: Theoret. Chim. Acta (Berl.) **62**, 107 (1982)
9. Leonard, J. M., Luken, W. L.: Int. J. Quantum Chem. **25**, 355 (1984)
10. Wigner, E. P., Seitz, F.: Phys. Rev. **43**, 804 (1933); **46**, 509 (1934)
11. Slater, J. C.: Phys. Rev. **81**, 385 (1951)
12. Sperber, G.: Int. J. Quantum Chem. **5**, 177, 189 (1971); **6**, 881 (1972)
13. Boyd, R. J., Coulson, C. A.: J. Phys. B **7**, 1805 (1974)
14. Cooper, I. L., Pounder, N. M.: Int. J. Quantum Chem. **17**, 759 (1980)
15. Luken, W. L., Beratan, D. N.: Theoret. Chim. Acta (Berl.) **61**, 265 (1982)
16. Luken, W. L.: Int. J. Quantum Chem. **22**, 889 (1982)
17. Magnasco, V., Perico, A.: J. Chem. Phys. **47**, 971 (1967)
18. Verwoerd, W. S.: Chem. Phys. **44**, 151 (1979)
19. Claxton, T. A.: Chem. Phys. **52**, 23 (1980)

20. Diner, S., Malrieu, J. P., Claverie, P., Jordan, F.: Chem. Phys. Lett. **2**, 319 (1968)
21. Diner, S., Malrieu, J. P., Claverie, P.: Theoret. Chim. Acta (Berl.) **13**, 1 (1969)
22. Malrieu, J. P., Claverie, P., Diner, S.: Theoret. Chim. Acta (Berl.) **13**, 18 (1969)
23. Diner, S., Malrieu, J. P., Jordan, F., Gilbert, M.: Theoret. Chim. Acta (Berl.) **15**, 100 (1969)
24. Jordan, F., Gilbert, M., Malrieu, J. P., Pincelli, U.: Theoret. Chim. Acta (Berl.) **15**, 211 (1969)
25. Cullen, J. M., Zerner, M. C.: Int. J. Quantum Chem. **22**, 497 (1982)
26. Löwdin, P.-O.: Phys. Rev. **97**, 1474 (1955); Adv. Chem. Phys. **2**, 207 (1959)
27. Luken, W. L., Beratan, D. N.: Electron Correlation and the Chemical Bond. Durham, NC: Freewater Productions, Duke University, 1980
28. Luken, W. L., Culberson, J. C.: Int. J. Quant. Chem. Symp. **16**, 265 (1982)
29. Luken, W. L., Culberson, J. C.: in Local Density Approximations in Quantum Chemistry and Solid State Physics, Dahl, J. P., Avery, J., Eds., New York: Plenum 1984
30. Daudel, R.: Compt. Rend. Acad. Sci. **237**, 601 (1953)
31. Daudel, R., Brion, H., Odoit, S.: J. Chem. Phys. **23**, 2080 (1955)
32. Ludeña, E. V.: Int. J. Quantum Chem. **9**, 1069 (1975)
33. Bader, R. F. W., Stephens, M. E.: J. Amer. Chem. Soc. **97**, 7391 (1975)
34. Löwdin, P.-O.: J. Chem. Phys. **18**, 365 (1950)
35. Kleier, D. A., Halgren, T. A., Hall, J. H., Lipscomb, W.: J. Chem. Phys. **61**, 3905 (1974)
36. Baldwin, S. W., Wilkinson, J. M.: Tetrahedron Lett. **20**, 2657 (1979)
37. Baldwin, S. W., Fredericks, J. E.: Tetrahedron Lett. **23**, 1235 (1982)
38. Baldwin, S. W., Blomquist, H. R.: Tetrahedron Lett. **23**, 3883 (1982)
39. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
40. Herzberg, G.: in Molecular Spectra and Molecular Structure III, Electronic Spectra and Electronic Structure of Polyatomic Molecules, New York: Van Nostrand Reinhold, 1966
41. Synder, L. C., Basch, H.: in Molecular Wavefunctions and Properties, New York: Wiley-Interscience, 1972
42. Eliel, E. L., Allinger, N. L., Angyal, S. J., Morrison, G. A.: Conformational Analysis, New York: Wiley-Interscience, 1965
43. Williams, J. E., Stang, P. J., Schleyer, P.: Ann. Rev. Phys. Chem. **19**, 531 (1968)
44. Sinanoğlu, O., Skutnik, B.: Chem. Phys. Lett. **1**, 699 (1968)
45. Kutzelnigg, W.: Israel J. Chem. **19**, 193 (1980)
46. Schindler, M., Kutzelnigg, W.: J. Chem. Phys. **76**, 1919 (1982)
47. Nafie, L. A., Polaravapu, P. L.: J. Chem. Phys. **75**, 2935 (1981)
48. Lavery, R., Etchebest, C., Pullman, A.: Chem. Phys. Lett. **85**, 266 (1982)

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