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Localized Orbitals and the Fermi Hole

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The relationship between localized orbitals and the Fermi hole is demonstrated with contour maps of the Fermi hole in the water molecule. These contour maps indicate the presence of regions in which the Fermi hole is relatively stable, regions in which the shape of the Fermi hole changes rapidly, and regions in which the Fermi hole follows the probe electron smoothly. If a single orbital dominates any region of space, the Fermi hole resembles that orbital for any position of the probe electron in the dominated region.

Key words: Localized orbitals–Fermi hole.

1. Introduction

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]. These invariant properties include the total electronic energy and the first and second order reduced density matrices [2–4], as well as others. Because of this invariance, any of these properties may be described equally well using either canonical self-consistent field (SCF) orbitals, or the corresponding localized SCF orbitals [5–7].

This paper considers the relationships between localized molecular orbitals and the Fermi hole [8–16]. The relationship between the Fermi hole, the localizability of electrons, and the theory of loges [17, 18] have been examined previously by Bader and co-workers [19–22]. In this paper, the relationship between the Fermi hole and localized molecular orbitals is demonstrated in a sequence of contour maps of the Fermi hole in the water molecule. Being invariant to a

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Offprint requests and correspondence to: W. L. Luken unitary transformation of the occupied orbitals, the Fermi hole may be determined directly in terms of canonical SCF molecular orbitals. As a result, it is possible to obtain information about the localizability of the orbitals in an SCF wavefunction without transforming canonical orbitals to localized orbitals, without choosing a criterion of localization, and without partitioning a molecule into regions.

The characteristics of localized orbitals are reviewed briefly in the following section of this paper. The third section provides a definition of the Fermi hole as used in this work. The contour maps of the Fermi hole in the water molecule are presented in the fourth section. This is followed by a discussion of the relationship between the Fermi hole and localized orbitals.

2. Localized Orbitals

An N electron Slater determinant is an anti-symmetric product of N spin-orbitals,

$$\Phi(1, 2, \cdots N) = \hat{A}[\phi_1(1)\phi_2(2) \cdots \phi_N(N)]. \tag{1}$$

The operator $\hat{A}$ is the N electron anti-symmetrizer, and the space and spin co-ordinates of each electron are specified by the corresponding electronic index. Each of the spin–orbitals in this product is usually formed as the product of a spatial function and a spin function (α or β),

$$\phi_i(1) = \begin{cases} f_i(\vec{r}_1)\alpha_1; & 1 \leq i \leq n \\ f_i(\vec{r}_1)\beta_1; & n < i \leq N \end{cases}$$

where n is the number of electrons with α spin. In the case of a closed shell Slater determinant, we have $n = N/2$ and $f_i(\vec{r}) = f_{i+n}(\vec{r})$.

The SCF orbitals for the single determinantal wavefunctions Φ are determined by the spatial functions $f_i(\vec{r})$ which minimize the energy of Φ subject to constraints of orbital orthonormality. These functions are usually determined as the eigenfunctions of appropriate Fock operators [23–26]. The resulting canonical SCF orbitals may be widely distributed over distant parts of a molecule.

Alternatives to the canonical SCF orbitals may be determined by taking advantage of the invariance of a Slater determinant to a unitary transformation of the occupied orbitals. In particular, it is possible to define localized orbitals which are related to the canonical SCF orbitals by a unitary transformation, and which satisfy some criteria of localization. Several criteria for determining localized orbitals have been proposed. These include maximization of the sum of orbital self-repulsion integrals [5, 7]

$$S_1 = \sum_{i=1}^{n} \langle ii|1/r_{12}|ii\rangle, \tag{3}$$

minimization of the sum [27]

$$S_2 = \sum_{i=1}^{n} \langle ii|r_{12}{}^2|ii\rangle, \tag{4}$$

and maximization of the sum [28]

$$S_3 = \sum_{i=1}^{n} \langle ii|\delta(r_{12})|ii\rangle. \tag{5}$$

The localized orbitals determined by each of these criteria generally differ from those determined by the other criteria, but the differences are usually very minor [29, 30]. It is usually easy to interpret each of the resulting localized orbitals as a core orbital, lone pair (atomic hybrid) orbital, or chemical bond [31–34]. Consequently, these orbitals provide an appealing basis for the description of molecular structure and bonding. In addition, there has been much interest in the use of localized orbitals for the description of electron correlation in molecules [35–42].

In spite of the useful features characteristic of localized orbitals, it is possible to regard them as arbitrary and artificial. Each of the types of localized orbitals considered above depends upon a criterion of localization which is necessarily dependent upon unitary transformations of the occupied SCF orbitals. Consequently, these criteria cannot correspond to observable properties of the N electron SCF wavefunction. These artificial criteria are then imposed upon the SCF orbitals, which must always comply to some degree.

The curious fact is that the various criteria for determining localized orbitals all tend to yield very similar results. If there were no sound physical basis for the concept of localized orbitals, then the orbitals determined by each criterion should frequently be grossly inconsistent with those determined by the other criteria. The weakness of the dependence of localized orbitals on the criterion of localization suggests the existence of a common element which is independent of these criteria.

3. Density Functions and the Fermi Hole

The first order reduced density matrix for the wavefunction in Eq. (1) is given by [2–4]:

$$\gamma(1;2) = \rho_\alpha(r_1; r_2)\alpha_1\alpha_2^* + \rho_\beta(r_1; r_2)\beta_1\beta_2^* \tag{6}$$

where

$$\rho_\alpha(r_1; r_2) = \sum_{i=1}^{n} f_i(r_1)f_i^*(r_2) \tag{7a}$$

is the spatial density of electrons with α spin, and

$$\rho_\beta(r_1; r_2) = \sum_{i=n+1}^{N} f_i(r_1)f_i^*(r_2) \tag{7b}$$

is the corresponding density for electrons with β spin. The total spatial electronic density is given by

$$\rho(r_1; r_2) = \rho_\alpha(r_1; r_2) + \rho_\beta(r_1; r_2). \tag{8}$$

In the special case of a closed shell electronic configuration, the α and β density matrices each equal half of the total density.

The Fermi hole may be defined as

$$\Delta(r_1; r_2) = \rho(r_1) - 2\rho_2(r_1, r_2)/\rho(r_2) \tag{9}$$

where $\rho(r) = \rho(r; r)$. This definition differs from more conventional definitions by a factor of -1 [10, 11, 14, 15]. The definition adopted here yields a positive Fermi hole, facilitating comparison with orbital density functions. ρ_2 is the two electron density function given by [3, 13, 14]

$$\rho_2(r_1, r_2) = \rho_{\alpha\alpha}(r_1, r_2) + \rho_{\alpha\beta}(r_1, r_2) + \rho_{\beta\alpha}(r_1, r_2) + \rho_{\beta\beta}(r_1, r_2). \tag{10}$$

In the case of a single Slater determinant, we have

$$\rho_{\alpha\alpha}(r_1, r_2) = [\rho_\alpha(r_1)\rho_\alpha(r_2) - \rho_\alpha(r_1, r_2)\rho_\alpha(r_2, r_1)]/2, \tag{11a}$$

$$\rho_{\alpha\beta}(r_1, r_2) = \rho_\alpha(r_1)\rho_\beta(r_2)/2, \tag{11b}$$

and $\rho_{\beta\alpha}$ and $\rho_{\beta\beta}$ are given by analogous expressions. In the case of a closed shell electronic configuration,

$$\rho_2(r_1, r_2) = [\rho(r_1)\rho(r_2) - \rho(r_1; r_2)\rho(r_2; r_1)/2]/2. \tag{12}$$

Consequently, the Fermi hole for a closed shell electronic configuration is given by

$$\Delta(r_1; r_2) = \rho(r_1; r_2)\rho(r_2; r_1)/2\rho(r_2). \tag{13}$$

In terms of individual orbitals, the closed shell Fermi hole is given by

$$\Delta(r_1, r_2) = \sum_{i=1}^{n} d_i(r_1)P_i(r_2) + 2 \sum_{\substack{i=1 \\ (i \neq j)}}^{n} \sum_{j=1}^{n} S_{ji}(r_1)S_{ij}(r_2)/\rho(r_2), \tag{14}$$

where

$$S_{ij}(r) = f_i^*(r)f_j(r), \tag{15}$$

$$d_i(r) = S_{ii}(r) = |f_i(r)|^2, \tag{16}$$

and

$$P_i(r) = 2\, d_i(r)/\rho(r). \tag{17}$$

The quantity $P_i(r)$ specifies the probability that an electron at position r is in orbital f_i [9]. The sum of these probabilities is equal to unity,

$$\sum_{i=1}^{n} P_i(r) = 1, \tag{18}$$

for all values of r. The quantity $S_{ij}(r)$ is an overlap integrand, and integrates to zero for $i \neq j$ (for orthonormal orbitals).

In the case of an open shell Slater determinant, the Fermi hole for the α electrons differs from that of the β electrons. In this case the α spin Fermi hole may be defined as

$$\Delta_\alpha(r_1; r_2) = \rho_\alpha(r_1) - 2\rho_{\alpha\alpha}(r_1, r_2)/\rho_\alpha(r_2), \tag{19}$$

and an analogous expression may be defined for the β spin Fermi hole. In terms of individual orbitals, this is given by

$$\Delta_\alpha(r_1; r_2) = \sum_{i=1}^{n} d_i(r_1)P_i(r_2) + \sum_{\substack{i=1 \\ (i \neq j)}}^{n} \sum_{j=1}^{n} S_{ji}(r_1)S_{ij}(r_2)/\rho_\alpha(r_2). \tag{20}$$

In the case of a closed shell electronic configuration, this is identical to the Fermi hole defined in Eq. (14).

The Fermi hole defined by Eqs. (14) and (20) is regarded as a function of r_1 which depends parametrically on the position r_2 of a "probe electron". This function of r_1 describes the loss of density from the total electronic density distribution (for electrons of like spin) associated with the presence of the probe electron at position r_2.

The Fermi hole defined by Eq. (9) may also be written as

$$\Delta(r_1; r_2) = \sum_i \sum_j \Delta_{ij}(r_2) f_i(r_1) f_j^*(r_1) \tag{21}$$

where $\Delta_{ij}(r_2)$ is an element of a matrix $\mathbf{\Delta}(r_2)$ which depends on the position of the probe electron. This may be expressed in the diagonal form

$$\Delta(r_1; r_2) = \sum_k M_k(r_2) |g_k(r_1; r_2)|^2 \tag{22}$$

where the $M_k(r_2)$ are the eigenvalues of $\mathbf{\Delta}(r_2)$ and $g_k(r_1; r_2)$ is a Fermi hole natural orbital, or Fermi orbital. The eigenvalues sum to unity

$$\sum_k M_k(r_2) = 1, \tag{23}$$

following the sign convention adopted above.

In the case of a closed shell SCF wavefunction, the elements of $\mathbf{\Delta}(r_2)$ are given by

$$\Delta_{ij}(r_2) = 2\, S_{ij}(r_2)/\rho(r_2). \tag{24}$$

Consequently, the eigenvalues of $\mathbf{\Delta}$ are all equal to zero, except for one which is equal to unity. In this case, the Fermi hole is determined by a single Fermi orbital

$$\Delta(r_1; r_2) = |g(r_1; r_2)|^2, \tag{25}$$

where

$$g(r_1; r_2) = \sum_{i=1}^{n} f_i(r_1)[f_i^*(r_2)/f(r_2)] \tag{26}$$

and

$$f(r) = \sqrt{\rho(r)/2.} \tag{27}$$

The Fermi orbital $g(r_1; r_2)$ is a specific linear combination of the occupied orbitals $f_i(r_1)$. As such it may be positive or negative, and it may possess nodes. Therefore, the Fermi hole for a single Slater determinant is capable of possessing nodes. This is in contrast to the Fermi hole for a correlated wavefunction (Eqs. (21) and (22)) which generally cannot possess nodal surfaces.

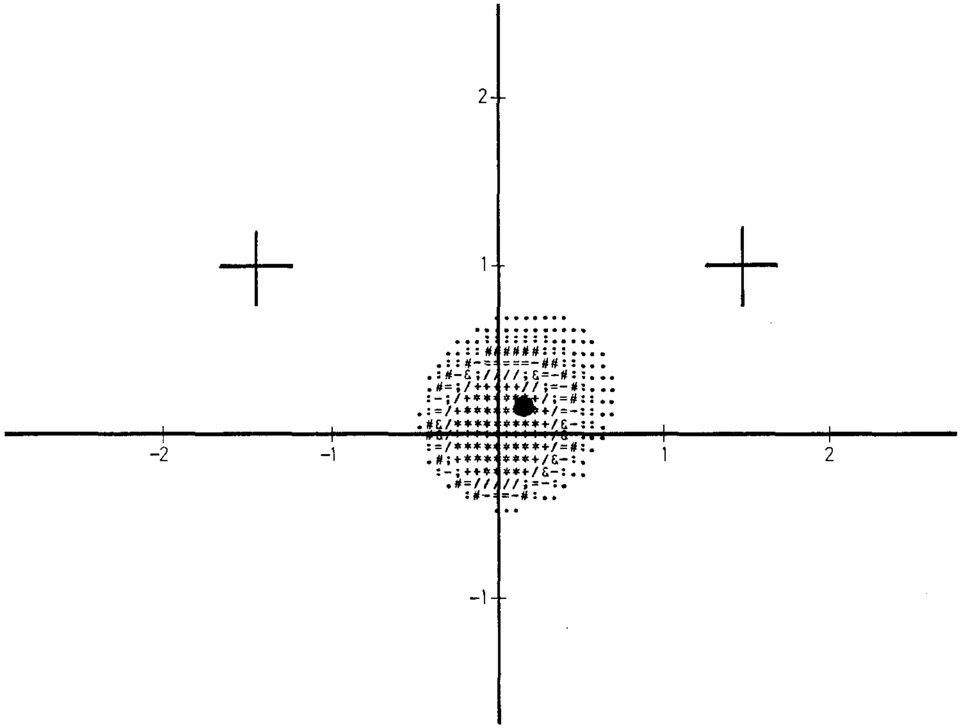

Fig. 1. The Fermi hole in the plane of the nuclei of a water molecule. The oxygen nucleus is located at the origin and the protons (+) are located at $x = \pm 1.515263$ Bohr and $y = 1.049898$ Bohr. The position of the probe electron ($X = 0.18$ Bohr, $y = 0.20$ Bohr) is indicated by a solid circle. The range of densities represented by each symbol is given by 0 (blank) 0.025 (.) 0.05 (:) 0.10 (#) 0.15 (−) 0.20 (=) 0.30 (&) 0.40 (;) 0.50 (/) 1.00 (+) 2.00 (*) higher; in units of electrons per cubic Bohr. For comparison, the electronic density of a hydrogen atom at the Bohr radius is $1/\pi e^2 = 0.043$ electrons per cubic Bohr

4. The Fermi Hole in the Water Molecule

The shape of the Fermi hole in the water molecule for each of six positions of the probe electron is shown in Figs. 1 to 6. These contour maps are based on a double zeta SCF wavefunction for the ground electronic state of the water molecule [43]. Figs. 1 through 5 show the shape of the Fermi hole in the plane of the nuclei. Fig. 6 is based on the plane perpendicular to the plane of the nuclei which contains the C_2 rotation axis. A collection of approximately 100 similar contour maps based on an STO-3G SCF wavefunction [44] has been used to produce an animated movie of the Fermi hole in a water molecule [45].

Figure 1 shows the shape of the Fermi hole when the probe electron is relatively close to the oxygen nucleus. This Fermi hole is nearly entirely contained within the oxygen atom inner (*K*) shell. Any position of the probe electron closer to the nucleus than this is expected to yield a Fermi hole which is nearly identical to this. That is, the shape of the Fermi hole is relatively insensitive to the position of the probe electron when it is within roughly 0.3 Bohr of the oxygen nucleus. This is consistent with the observation of Sperber who noted that the Fermi hole of the beryllium atom tends to be confined to the *K* shell of this atom when the probe electron is within the region dominated by the *K* shell orbital [11].

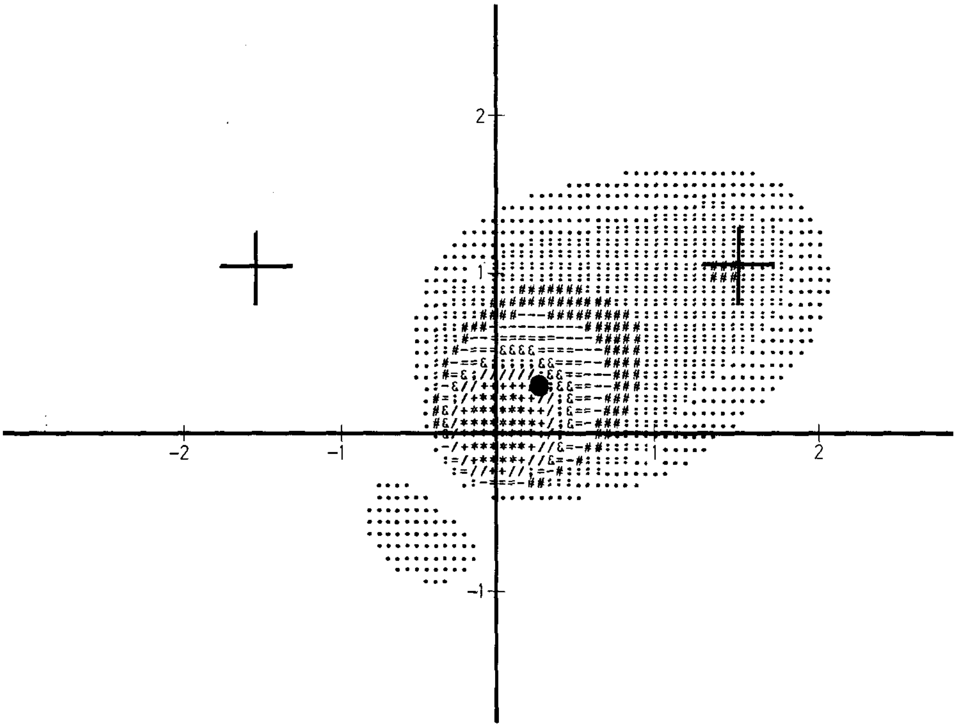

Fig. 2. Same as Fig. 1, except tha the probe electron is located at ($x = 0.27$ Bohr, $y = 0.30$ Bohr)

The position of the probe electron in Fig. 2 is only 0.135 Bohr away from the position in Fig. 1. As the probe electron moves in this direction (from the position in Fig. 1), the Fermi hole rapidly extends into the vicinity of one of the hydrogen atoms. In this case, the shape of the Fermi hole is very sensitive to the position of the probe electron.

The rapid changes in the shape of the Fermi hole characterized by Fig. 2 are nearly complete by the time the probe electron reaches the position in Fig. 3. This position is roughly 0.40 Bohr from the position in Fig. 2 and 0.81 Bohr from the oxygen nucleus. Further changes in the position of the probe electron beyond this point, as demonstrated in Figs. 4 and 5, yield relatively small changes in the shape of the Fermi hole. As in Fig. 1, the shape of the Fermi hole shown in Figs. 3, 4 and 5 is relatively insensitive to the position of the probe electron. Comparison to Fig. 7 shows that the relatively stable shape which appears in Figs. 3, 4, and 5 bears a strong resemblance to the localized molecular orbital (determined by Boys' criterion) associated with the O—H bond.

Figure 6 shows the shape of the Fermi hole for a probe electron located in the region normally associated with the oxygen lone pairs. Comparison with Fig. 8 shows that this Fermi hole is very similar to the corresponding localized molecular orbital determined by the Boys' criterion. As in Figs. 3, 4, and 5, the Fermi hole

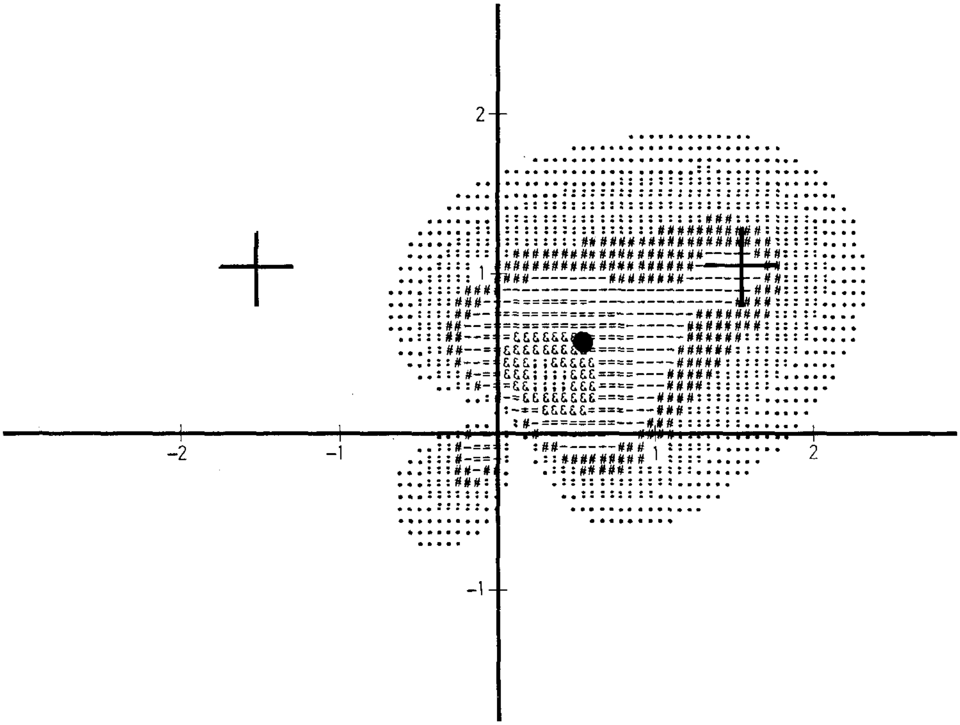

Fig. 3. Same as Fig. 1, except that the probe electron is located at ($x = 0.54$ Bohr, $y = 0.60$ Bohr)

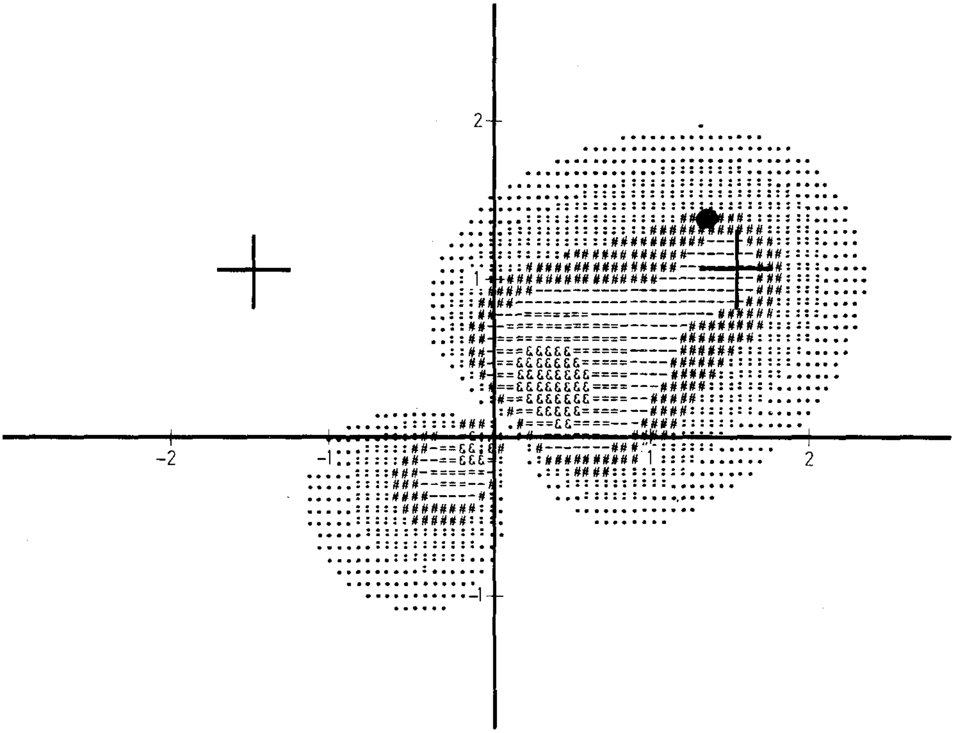

Fig. 4. Same as Fig. 1, except that the probe electron is located at ($x = 1.38$ Bohr, $y = 1.425$ Bohr)

shown in Fig. 6 includes the nodal surface found in the corresponding localized molecular orbital.

The shape of the Fermi hole shown in Fig. 6 is insensitive to radial displacement of the probe electron away from the oxygen atom. As the probe electron moves radially towards the oxygen atom, the shape of the Fermi hole is expected to be relatively stable until the probe electron is less than roughly 0.8 Bohr from the oxygen nucleus. When the probe electron is between 0.8 and 0.3 Bohr, the Fermi hole is expected to change rapidly from the shape shown in Fig. 6 to that of Fig. 1. When the probe electron is less than 0.3 Bohr, the shape of the Fermi hole will again be relatively stable.

The response of the Fermi hole to angular motion of the probe electron in Fig. 6 differs greatly from that described above for radial motion. For angular motion of the probe electron between the position indicated in Fig. 6, and the symmetrically related position below the molecular plane, the Fermi hole follows the probe electron smoothly and synchronously. There is almost no change in the shape of the Fermi hole, but this nearly rigid shape rotates about the oxygen nucleus following the probe almost perfectly as the angular position of the probe electron changes. As such, the shape of the Fermi hole can be changed from one of the lone pairs to the other lone pair through a nearly rigid rotation which

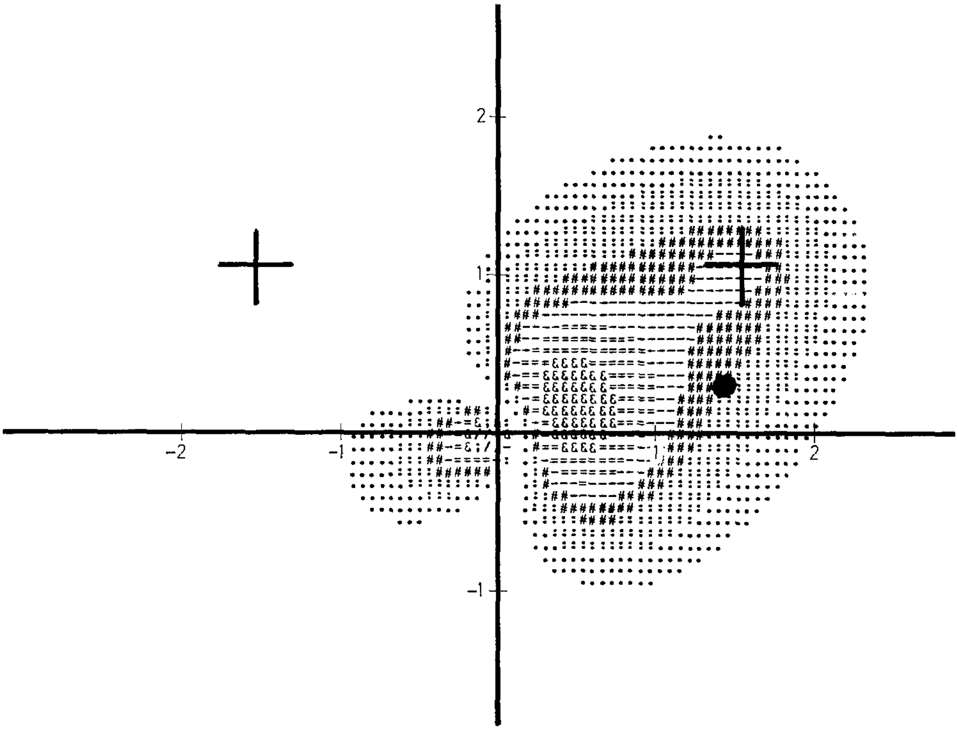

Fig. 5. Same as Fig. 1, except that the probe electron is located at ($x = 1.40$ Bohr, $y = 0.30$)

recognizes no boundaries separating the lone pairs. This contrasts with the bond to core or lone pair to core transformations which display regions of relative stability separated by regions in which the shape of the Fermi hole changes rapidly. Likewise, the bond to bond transformation cannot proceed by a rigid rotation of an O—H bond because the protons are fixed in space and the shapes of the O—H bonds are determined by the positions of the protons.

5. Localized Orbitals and the Fermi Hole

The Fermi hole in the water molecule exhibits three distinctive types of behavior:

1. The Fermi hole may follow the motion of the probe electron rigidly.
2. The Fermi hole may be insensitive to the position of the probe electron.
3. The Fermi hole may change rapidly in response to small changes in the position of the probe electron.

The first type of behavior is characteristic of a uniform density free electron gas. Such a system is translationally invariant and the size and shape of the Fermi hole cannot depend on the position of the probe electron. The Fermi hole is locked onto the probe electron and follows it like a rigid object. Any other system which is translationally or rotationally invariant must exhibit similar characteristics. For example, the size and shape of the Fermi hole in a closed

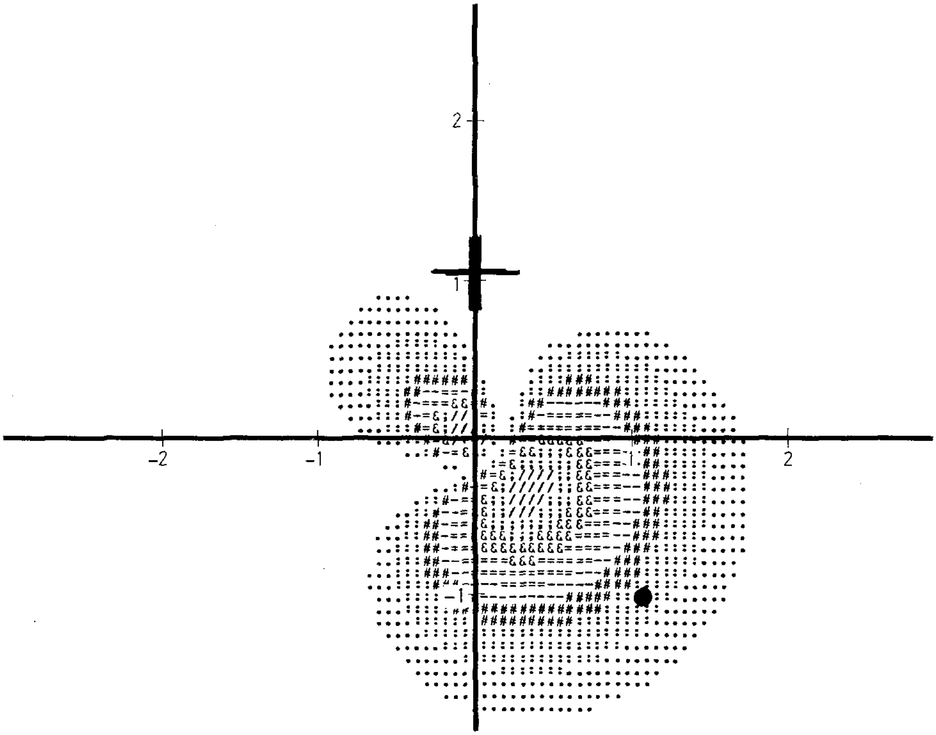

Fig. 6. Same as Fig. 1, except that the probe electron is located at ($x = 0.0$, $y = -1.0$, $z = 1.0$) and the density is plotted for the yz plane (perpendicular to molecular plane and including the C_2 axis)

shell atom is invariant with respect to the angular co-ordinates of the probe electron. Likewise, the shape of the Fermi hole in a linear molecule is invariant to rotation of the probe electron about the molecular axis. The Fermi hole in a highly conjugated molecule should exhibit this type of behavior to the extent that the (pi) electrons may be described by a free electron gas. This type of behavior is characteristic of delocalized electrons.

The second and third types of behavior may be explained with the help of an isolated orbital model. Consider a partition of the electronic position space into n distinct non-overlapping regions $\Omega_1, \Omega_2, \ldots, \Omega_n$. These regions may be similar to the loges advocated by Daudel and co-workers [17–19]. Allow each region Ω_i to contain a single normalized spatial function $f_i(r)$ which is zero at all points not contained in Ω_i. In this situation, the quantities $S_{ij}(r)$ in Eqs. (14) and (20) vanish everywhere for all $i \neq j$. In addition, the probabilities $P_i(r)$ vanish for all points not in Ω_i, and equal unity for all points in Ω_i. Consequently, the Fermi hole is given by

$$\Delta(r_1; r_2) = d_i(r_1), \quad \text{for } r_2 \text{ in } \Omega_i. \tag{28}$$

In this model, the shape of the Fermi hole is independent of the position of the probe electron as long as the probe electron remains within a single region. As

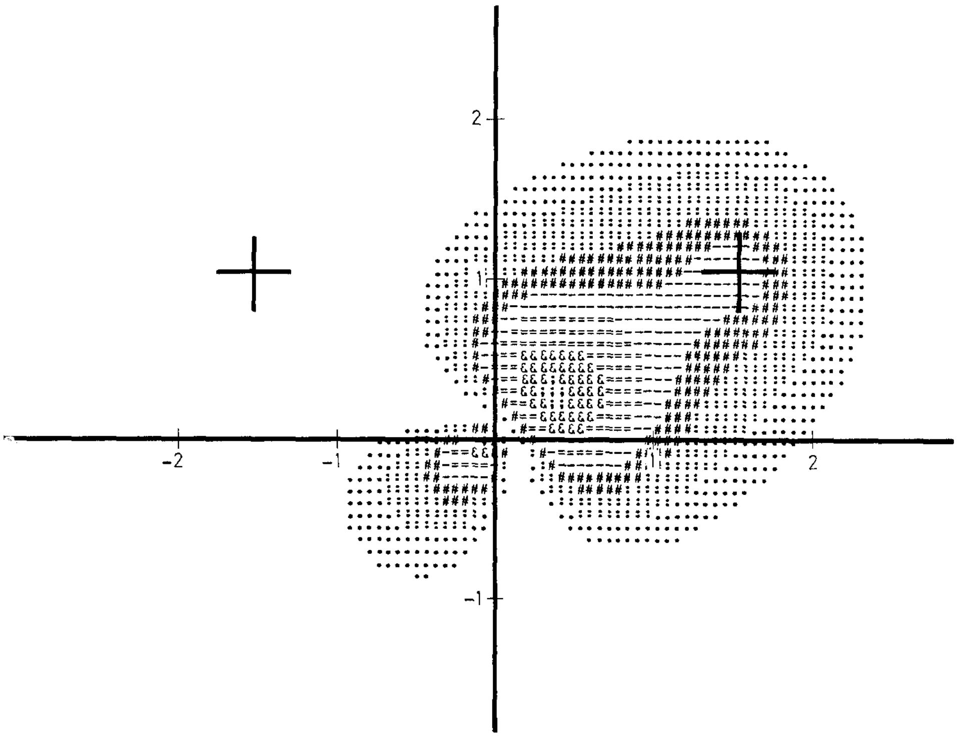

Fig. 7. Localized molecular orbital determined by Boys' criterion. The O—H bond in the plane of the molecule. The contours are defined in Fig. 1

soon as the probe electron crosses a boundary from one region into another, the shape of the Fermi hole changes discontinuously from one shape to that required by the new region.

The situation described above may be realized by a collection of widely separated helium atoms (or hydrogen molecules). For example, consider a set of eight helium atoms located at the corners of a very large cube. The canonical SCF molecular orbitals of this system would have the symmetries of irreducible representations of the 0_h point group. The localized SCF molecular orbitals would consist of an atomic SCF orbital for a helium atom at each corner of the cube. The Fermi hole, however, is invariant to the choice of localized or canonical

or any of their properties. No matter what choice of orbitals is used to describe the Fermi hole, the Fermi hole will always describe the localized orbitals.

In the case of a molecular SCF wavefunction, it is not generally possible to isolate the individual orbitals into isolated regions. Each orbital, even when localized, penetrates the regions dominated by other orbitals. Consequently, the simple isolated orbital model discussed above cannot describe the behavior of the Fermi hole in a typical molecule. In most molecules, however, the features

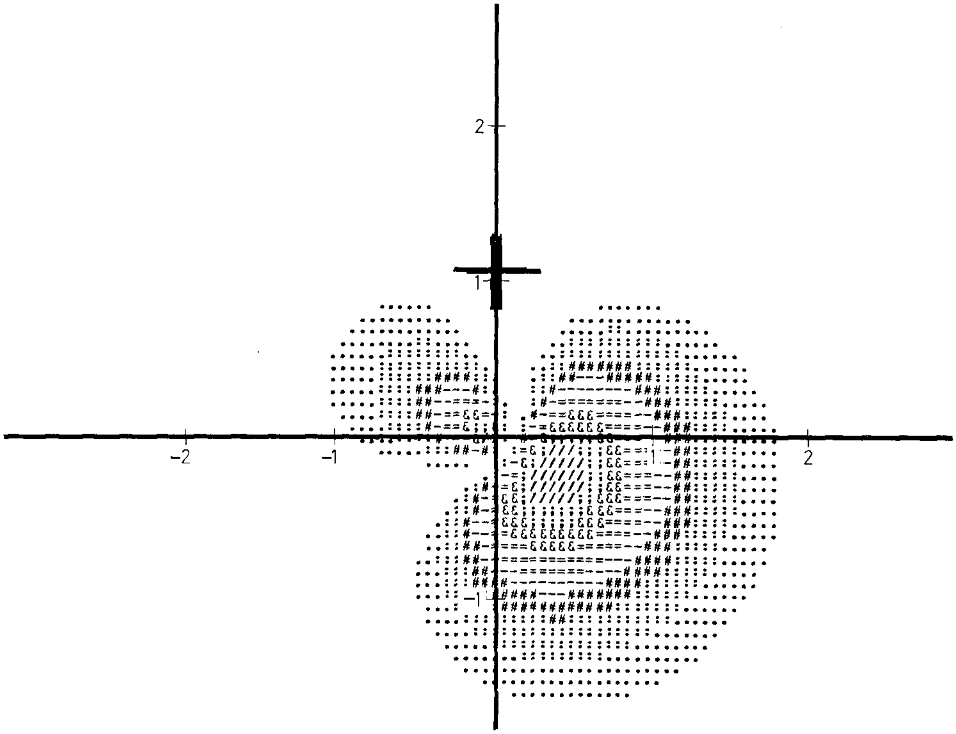

Fig. 8. Localized molecular orbital determined by Boys' criterion. One of the oxygen lone pair orbitals, plotted in the plane specified in Fig. 6. The contours are defined in Fig. 1

of the isolated orbital model are not destroyed entirely, but survive in a modified form. Thus, instead of sharply defined regions within which the Fermi hole is independent of the position of the probe electron, there are regions within which the Fermi hole is weakly dependent on the position of the probe electron. Instead of sharply defined boundaries at which the Fermi hole changes discontinuously, there are fuzzy regions within which the shape of the Fermi hole changes rapidly. Instead of following the probe electron smoothly, the Fermi hole may lag behind and then jump ahead as the probe electron passes through a boundary region.

The regions of stability are the regions where a single orbital dominates the charge density. Eq. (28) is a good approximation in such regions, and the shape of the Fermi hole for a probe electron in one of these regions is largely determined by the orbital which dominates this region. The condition that a single orbital dominates any region of space is satisfied best for localized molecular orbitals. It is not necessary to use localized orbitals to evaluate the Fermi hole because the Fermi hole is invariant to unitary transformations of the occupied orbitals. Consequently, if there exists any orbital which dominates a certain region of space, and which is a member of a set of orbitals related to the canonical SCF orbitals by a unitary transformation, then the Fermi hole will resemble that orbital for any position of the probe electron within that region.

In the case of the water molecule, the region within roughly 0.3 Bohr of the oxygen nucleus is dominated by the oxygen inner shell orbital. Likewise, the region near each of the protons is dominated by a single O—H bond localized orbital. Between each of these regions there is a boundary region within which the size and shape of the Fermi hole changes rapidly.

The side of the water molecule opposite to the protons is dominated by two lone pair localized orbitals, each of which is well approximated by an sp^3 hybrid atomic orbital. This side of the oxygen atom resembles half of a neon atom. As such, the charge distribution in this region is almost rotationally invariant. Consequently, it is possible for the Fermi hole to follow the probe electron from one lone pair to the other with no intervening boundaries being crossed. Thus, we have a set of four electrons delocalized in the region of the two lone pair orbitals.

Although the lone pair region does not exhibit stability with respect to angular motion of the probe electron, this region, as well as the O—H bond regions display stability with respect to radial motion of the probe electron as it moves away from the oxygen nucleus and into the fringe areas of the electronic distribution. This is caused by the fact that the magnitude of the Fermi hole is limited to less than or equal to half of the total density at any point, and the integrated magnitude of the Fermi hole must always equal unity. As such, the Fermi hole cannot follow the probe electron into the fringe areas of the electronic distribution. The necessary contributions to the integrated Fermi hole do not exist beyond a certain point. Once the Fermi hole has consumed most of the available electron density in any fringe area, it is essentially stuck, and further radial motion of the probe electron does not matter.

The stability of the Fermi hole for certain regions of the position of the probe electron can also be explained through Eqs. 25 to 27. Allow each of the SCF orbitals $f_i(r)$ to be determined by a linear combination of functions $\chi_\mu(r)$,

$$f_i(r) = \sum_\mu C_{i\mu}\chi_\mu(r). \tag{29}$$

The functions $\chi_\mu(r)$ may be either conventional Slater type or Gaussian basis functions, or they may be idealized atomic orbitals. Consider the situation where region Ω_μ is dominated by the function $\chi_\mu(r)$. That is, the magnitude of $\chi_\mu(r)$ is much greater than that of all of the other basis functions for any point in the region Ω_μ. In this case, we have

$$f_i(r) \cong C_{i\mu}\chi_\mu(r), \tag{30}$$

and

$$f(r) \cong C_\mu\chi_\mu(r), \tag{31}$$

for r in Ω_μ, and

$$g(r_1; r_2) \cong g_\mu(r_1) \equiv \sum_{i=1}^{n} C_{i\mu} f_i(r_1)/C_\mu, \tag{32}$$

for r_2 in Ω_μ, where

$$C_\mu^2 = \sum_{i=1}^{n} |C_{i\mu}|^2. \tag{33}$$

Therefore, if any atomic orbital dominates any region of space, the Fermi orbital g, and thus the Fermi hole, is independent of the position of the probe electron as long as the probe electron is located within this region.

Based on the considerations presented above, the Fermi orbital g_μ should be a good approximation to one of the localized molecular orbitals for this molecule. This expectation is confirmed in Tables 1 and 2. Table 1 shows the double zeta orbitals used in this work. The Fermi orbitals determined by basis functions #1 and #5 are shown in Table 2. The corresponding localized molecular orbitals determined by Boys' criterion are also shown in Table 2 for comparison. The similarity between the Fermi orbitals and Boys' localized molecular orbitals is very satisfactory considering the approximations involved in Eq. (32).

One consequence of Eq. (32) is that the Fermi hole determined by a minimal basis set appears much more localizable than that determined by an extended basis set. It is much easier for a single basis function to dominate a region of space if it is not required to share anything with any similar basis function. Thus the transition between core and bond orbitals occurs more abruptly for the STO-3G wavefunctions [45] than it does with the double zeta wavefunction.

Equation (32) does not provide anything for lone pair orbitals because the lone pair region is not dominated by a single atomic orbital. These orbitals can be represented by using Eq. (26), and selecting two positions of the probe electron near where the lone pairs are expected to be found.

Table 1. Double zeta self-consistent field molecular orbitals for the water molecule. The geometry is described in Fig. 1. The double zeta basis set is taken from the work of Dunning (Ref. [43]). The SCF energy for this wavefunction is −76.00984 Hartrees

BF #Atom	A-ORB	Mo #1	MO #2	MO #3	MO #4	MO #5
1 HYDRGN-1	HYD-1S-1	0.000040	0.132500	0.253144	0.133633	0.0
2 HYDRGN-1	HYD-1S-2	−0.000183	0.007729	0.128386	0.061411	0.0
3 HYDRGN-2	HYD-1S-1	0.000040	0.132500	−0.253144	0.133633	0.0
4 HYDRGN-2	HYD-1S-2	−0.000183	0.007729	−0.128386	0.061411	0.0
5 OXYGEN	OX-1S-1	0.581012	−0.130941	0.0	0.044407	0.0
6 OXYGEN	OX-1S-2	0.461238	−0.181527	0.0	0.061989	0.0
7 OXYGEN	OX-2S-1	−0.000166	0.511096	0.0	−0.188614	0.0
8 OXYGEN	OX-2S-2	0.001877	0.460447	0.0	−0.249762	0.0
9 OXYGEN	OX-2P-1-X	0.0	0.0	0.0	0.0	0.727677
10 OXYGEN	OX-2P-2-X	0.0	0.0	0.0	0.0	0.410294
11 OXYGEN	OX-2P-1-Y	0.0	0.0	0.569277	0.0	0.0
12 OXYGEN	OX-2P-2-Y	0.0	0.0	0.178846	0.0	0.0
13 OXYGEN	OX-2P-1-Z	0.001591	0.117049	0.0	0.633273	0.0
14 OXYGEN	OX-2P-2-Z	−0.000453	0.032478	0.0	0.338846	0.0

Table 2. Comparison of localized molecular orbitals determined by Eq. (32) and the corresponding molecular orbitals determined by Boys' criterion. The oxygen inner shell orbital and O—H bond orbital determined by Eq. (32) (this work) are based on basis functions 5 (OX-1S-1) and 1 (HYD-1S-1/HYDRGN-1) respectively. The SCF molecular orbitals used to determine these orbitals are shown in Table 1

			Oxygen inner shell		O—H bond	
BF #	Atom	A-ORB	This work	Boys LMO	This work	Boys LMO
1	HYDRGN-1	HYD-1S-1	−0.019075	−0.004714	0.315430	0.309310
2	HYDRGN-1	HYD-1S-2	0.002687	0.001471	0.132298	0.119442
3	HYDRGN-2	HYD-1S-1	−0.019075	−0.004714	−0.090885	−0.048690
4	HYDRGN-2	HYD-1S-2	0.002687	0.001471	−0.073771	−0.062123
5	OXYGEN	OX-1S-1	0.597237	0.590170	−0.036117	−0.042983
6	OXYGEN	OX-1S-2	0.493117	0.475072	−0.049933	−0.069177
7	OXYGEN	OX-2S-1	−0.126240	−0.043855	0.134786	0.226038
8	OXYGEN	OX-2S-2	−0.117695	−0.040364	0.087605	0.172330
9	OXYGEN	OX-2P-1-X	0.0	0.0	0.0	0.0
10	OXYGEN	OX-2P-2-X	0.0	0.0	0.0	0.0
11	OXYGEN	OX-2P-1-Y	0.0	0.0	0.456865	0.402540
12	OXYGEN	OX-2P-2-Y	0.0	0.0	0.143530	0.126463
13	OXYGEN	OX-2P-1-Z	0.022972	0.015941	0.317456	0.317566
14	OXYGEN	OX-2P-2-Z	0.017633	0.009406	0.157196	0.152177

6. Conclusions

The Fermi hole, loge theory, and localized molecular orbitals are all closely related. If there exists any orbital which dominates a certain region of space, then the shape of the Fermi hole is similar to that orbital for any position of the probe electron within the dominated region. If a single atomic orbital dominates any region of a molecule, then the localized orbital which dominates that region is determined by a simple linear combination of the SCF molecular orbitals.

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