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Author's Review

Properties of the Fermi Hole in Molecules

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The Fermi hole is a direct consequence of the exclusion principle for electronic wavefunctions of atoms, molecules, and solid state structures. The shape of the Fermi hole is determined by a function which is parametrically dependent on the position of a probe electron. The natural representation of this function is determined by a set of Fermi hole natural orbitals and their occupation numbers. The Fermi hole for a wavefunction consisting of a single Slater determinant is given by the square of a Fermi orbital. The sensitivity of a Fermi orbital to the position of the probe electron is given by the Fermi hole mobility function. A set of Fermi orbitals can be used to transform a set of canonical SCF molecular orbitals into localized orbitals.

I. INTRODUCTION

The properties of the Fermi hole were first studied more than 50 years ago in the context of solid state physics.[1,2] This work was concerned with the properties of a free electron gas as a model for the conduction electrons in a metal. Subsequent consideration of the properties of the Fermi hole in atomic and molecular physics and solid state physics has played an important part in the development of the local exchange potential which is essential to the Hartree-Fock-Slater self-consistent field theory and the $X\alpha$ approximation.[3-7] The local exchange potential also plays an important role in local density functional theories.[8-10]

The properties of the Fermi hole in the electronic wavefunctions of atoms and molecules have been studied in several laboratories.[11-18] Most of these studies have been limited to atoms, molecules, or clusters of hydrogen atoms. Although Fermi correlation has been cited in qualitative descriptions of the electronic structure of molecules,[19] there has been very little quantitative information about the Fermi hole of molecules. One exception has been the work of Cooper and Pounder, who have tabulated various numerical quantities associated with correlation holes in certain small molecules.[17,18] Until recently,[20] however, no pictures of the Fermi hole in an electronic wavefunction of a stable polyatomic molecule had ever been published.

This article summarizes the recent progress in establishing the properties of the Fermi hole in the electronic wavefunctions of molecules.[21-23] Although this article is principally concerned with the properties of the Fermi hole, some properties of the Coulomb hole[24-29] are also considered. Following qualitative descriptions of the Fermi hole and the Coulomb hole, there is a discussion of the natural representations of the Fermi and Coulomb holes. Next, the sensitivity of the Fermi hole to the position of the probe electron is described in terms of the Fermi hole mobility function. Finally, the transformation of canonical SCF molecular orbitals to localized molecular orbitals based on the Fermi hole is presented.

2. DEFINITION OF THE FERMI HOLE AND THE COULOMB HOLE

The influence of an electron with spin t at position $\vec{r}_2$ on the probability of finding an electron with spin s at position $\vec{r}_1$ is given by the s—t correlation hole

$$\Delta_{st}(\vec{r}_1; \vec{r}_2) = \varrho_s(\vec{r}_1) - 2\,\varrho_2(\vec{r}_1, \vec{r}_2)/\varrho(\vec{r}_2), \tag{1}$$

where $\varrho_s(\vec{r}_1)$ is the s-spin electronic density function, and $\varrho_{st}(\vec{r}_1, \vec{r}_2)$ is the two-electron density function for electron 1 having spin s and electron 2 having spin t.[30-37] In addition, one may define the composite correlation hole as

$$\Delta(\vec{r}_1; \vec{r}_2) = \varrho(\vec{r}_1) - 2\,\varrho_2(\vec{r}_1, \vec{r}_2)/\varrho(\vec{r}_2), \tag{2}$$

which describes the influence of an electron at $\vec{r}_2$ on the probability of finding an electron at $\vec{r}_1$ irrespective of their spins.

The correlation holes $\Delta_{\alpha\beta}$ and $\Delta_{\beta\alpha}$ having $s = t$ are entirely the results of the coulombic repulsion between pairs of electrons. Consequently, it is appropriate to identify these functions with the Coulomb hole in the N electron wavefunction Ψ. The correlation holes $\Delta_{\alpha\alpha}$ and $\Delta_{\beta\beta}$ may each represent a combination of both Fermi correlation and coulombic interaction, and it is not necessarily possible to separate these two effects.[13,35]

In the case of a singlet electronic state, or other electronic state with $M_S = 0$, the distribution of electrons with α spin is identical to that of electrons with β spin. That is, $\varrho_\alpha = \varrho_\beta$. Likewise, the two electron density functions and the corresponding correlation holes are invariant with respect to reversal of both spins. In this case the composite correlation hole is simply the sum of the like-spin and unlike-spin correlation holes,

$$\Delta(\vec{r}_1; \vec{r}_2) = \Delta_{\alpha\alpha}(\vec{r}_1; \vec{r}_2) + \Delta_{\alpha\beta}(\vec{r}_1; \vec{r}_2). \tag{3}$$

This function, like $\Delta_{\alpha\alpha}$, represents a mixture of Fermi correlation and Coulombic interactions.

In the case of any wavefunction composed of a single Slater determinant the unlike-spin correlation holes $\Delta_{\alpha\beta}$ and $\Delta_{\beta\alpha}$ vanish for all values of $\vec{r}_1$ and $\vec{r}_2$. In these cases the like-spin correlation holes are entirely due to Fermi correlation, and they may be regarded as the definitions of the Fermi hole for wavefunctions composed of a single determinant. This condition applies to, but is not limited to, closed shell SCF wavefunctions. In the case of a closed shell SCF wavefunction the composite correlation hole Δ is identical to the

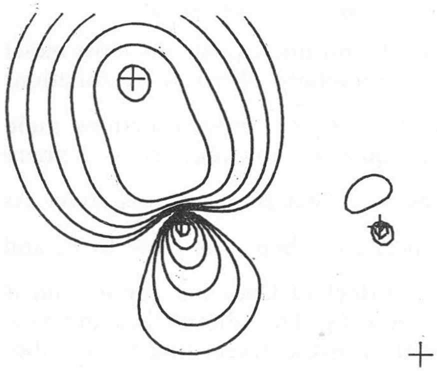

Figure 1.

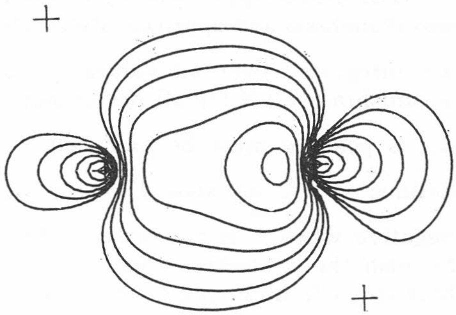

Figure 2.

Figure 1. A Fermi hole for a double zeta SCF wavefunction for the methanol molecule. The positions of a methyl proton (upper right), the carbon nucleus (left of center), the oxygen nucleus (right of center), and the hydroxyl proton (lower right) are each indicated by (+). The probe electron is located on the methyl proton. The contour lines indicated electronic densities of 0.005, 0.01 0.02, 0.04, 0.08, 0.16, 0.32, and 0.64 electrons per cubic bohr.

Figure 2. This is the same as Figure 1 except that the probe electron is located midway between the carbon and oxygen nuclei.

like-spin correlation hole $\Delta_{\alpha\alpha}$, and may used as the definition of the Fermi hole for a closed shell SCF wavefunction.

Figures 1, 2, and 3 indicate the shape of the Fermi hole for three positions of the probe electron in the methanol molecule. These figures are based on a closed shell SCF wavefunction determined by a double-zeta basis set.[38,39] The geometry was taken from the tabulation of Snyder and Basch.[40] The probe electron ($\vec{r}_2$) is located on one of the methyl protons in Figure 1, midway between the carbon and oxygen nuclei in Figure 2, and on the hydroxyl proton in Figure 3. When the probe electron is located on or near the carbon or oxygen nucleus the Fermi hole is much smaller and nearly spherical, centered on the nucleus and not on the probe electron.

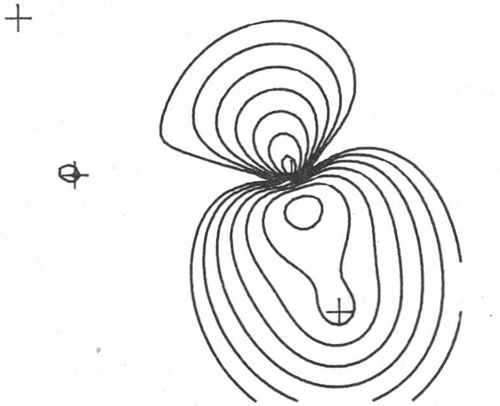

Figure 3. This is the same as Figure 1 except that the probe electron is located on the hydroxyl proton.

3. THE SIZE OF THE FERMI HOLE AND THE COULOMB HOLE

The unlike-spin correlation holes $\Delta_{\alpha\beta}$ and $\Delta_{\beta\alpha}$ do not vanish for most exact wavefunctions and approximate correlated wavefunctions. When these functions are integrated over all values of the first electron $(\vec{r}_1)$, these functions yield a vanishing result for all wavefunctions. Consequently, any regions of r_1 where $\Delta_{\alpha\beta}$ is positive must be balanced by regions of $\vec{r}_1$ where $\Delta_{\alpha\beta}$ is negative. As defined above, one should expect $\Delta_{\alpha\beta}$ to be positive when $\vec{r}_1$ is close to $\vec{r}_2$, and negative when $\vec{r}_1$ is far from $\vec{r}_2$. As such, the effect of Coulomb correlation is to push the β electrons away from the α electrons. This diminishes the probability of finding an α electron near a β electron, while preserving the number of α electrons.

Upon integration over all values of $\vec{r}_1$, the like-spin correlation holes $\Delta_{\alpha\alpha}$ and $\Delta_{\beta\beta}$ and the composite correlation hole Δ each yield a result of unity. Thus, instead of simply pushing the other electrons away, as is found for the unlike-spin correlation holes, these functions appear to represent the complete annihilation of one electron's worth of density. This 'lost' density represents the contribution from the electron at $\vec{r}_2$.

In the case of a single determinant wavefunction the like-spin correlation holes and the composite correlation hole are positive semi-definite functions of $\vec{r}_1$. In these cases these functions may be identified entirely with the corresponding Fermi holes. The maximum value attained by each of these functions at any point is limited by the total density of a given spin. These conditions, plus the fact that these functions must yield unity when integrated over all values of $\vec{r}_1$, limit the minimum spatial extent which may be realized by a Fermi hole.

Like the Fermi hole, a localized molecular orbital[41] must yield one electron's worth of density when integrated over all space. In addition, the maximum density represented by a localized molecular orbital is limited to the total density for each spin. Consequently, the localized molecular orbitals determined by an SCF wavefunction provide good estimates of the minimal spatial extent which may be expected of a Fermi hole. A localized orbital associated with a chemical bond usually spans the space between two or more nuclei. As a result, it may be necessary for a Fermi hole to encompass two or more atoms when the probe electron $(\vec{r}_2)$ is located in the region of a chemical bond. This is demonstrated in Figures 1 to 3, each of which shows a Fermi hole spanning two atoms. The Fermi hole is small compared to the distance between atoms only when the probe electron is located in a region of high density associated with innershell atomic orbitals.

The Fermi hole takes on an especially simple form for a singlet state of a two electron wavefunction, such as the ground electronic states of the helium atom and the hydrogen molecule. The two electron density functions $\varrho_{\alpha\alpha}$ and $\varrho_{\beta\beta}$ for these wavefunctions vanish because there is only one electron of each spin. If the position of this electron is specified, the probability of finding another one anywhere else is zero. In this case,

$$\Delta_{\alpha\alpha}(\vec{r}_1, \vec{r}_2) = \Delta_{\beta\beta}(\vec{r}_1, \vec{r}_2) = \varrho(\vec{r}_1)/2, \tag{4}$$

which is independent of $\vec{r}_2$. This condition applies to correlated wavefunctions as well as to the closed shell SCF wavefunctions for these states. Therefore, in contrast to a free electron gas,[1,2] the Fermi hole for an isolated pair of electrons does not follow the probe electron. Instead, the Fermi hole for an isolated pair of electrons remains fixed with respect to the nuclei (or the external potential) and does not depend on the location of the probe electron.

4. NATURAL REPRESENTATION OF CORRELATION HOLES

The natural representation of the s—t correlation hole is given by[21]

$$\Delta_{s,t}(\vec{r}_1; \vec{r}_2) = \Sigma_\mu \, n_\mu^{(s,t)}(\vec{r}_2) \, | g_\mu^{(s,t)}(\vec{r}_1; \vec{r}_2) |^2. \tag{5}$$

Likewise, the natural representation of the composite correlation hole is given by[21]

$$\Delta(\vec{r}_1; \vec{r}_2) = \Sigma_\mu \, n_\mu(\vec{r}_2) \, | g_\mu(\vec{r}_1; \vec{r}_2) |^2 \tag{6}$$

The functions $g_\mu^{(s,t)}$ and g_μ are the correlation hole natural orbitals, and the quantities $n_\mu^{(s,t)}$ and n_μ are the corresponding correlation hole natural orbital occupation numbers.

Values of the correlation hole natural orbital occupation numbers $n_\mu^{(\alpha,\beta)}$, $n_\mu^{(\alpha,\alpha)}$, and n_μ for the water molecule are shown in Table I. These values were determined by a multiconfigurational wavefunction based on a double-zeta basis set of atomic orbitals.[21] This wavefunction includes 85% of the correlation energy obtainable within this double-zeta basis set. The values shown in Table I were determined with the probe electron located on one of the protons.

TABLE I

Correlation Hole Natural Orbital Occupation Numbers. These Results Were Determined by a Correlated Wavefunction for the Water Molecule, with the Probe Electron Located on one of the Protons

$n^{\alpha,\beta}$ (H)	$n^{\alpha,\alpha}$ (H)	n (H)
0.12302	0.98861	1.01512
0.04273	0.01482	0.04883
0.02514	0.01188	0.03996
0.01930	0.00752	0.02654
0.00045	0.00592	0.00224
0.00023	0.00045	0.00044
—0.01904	—0.00383	—0.00885
—0.02534	—0.01085	—0.03553
—0.04335	—0.01461	—0.03996
—0.12309		—0.04879

The occupation numbers for the like-spin correlation holes and the composite correlation hole sum to unity, and those for the unlike-spin correlation holes sum to zero. In the case of a closed shell SCF wavefunction, the occupation numbers for the unlike-spin correlation holes all vanish, and the occupation numbers of the like-spin correlation holes and the composite correlation hole all vanish except for one which equals unity. In this case, the natural representation of the Fermi hole is the absolute square of the Fermi orbital[20-23]

$$\Delta(\vec{r}_1; \vec{r}_2) = |f(\vec{r}_1; \vec{r}_2)|^2. \tag{7}$$

The Fermi orbital is given by

$$f(\vec{r}_1; \vec{r}_2) = [2/\varrho(\vec{r}_2)]^{1/2} \Sigma_i\, g_i(\vec{r}_1)\, g_i(\vec{r}_2), \tag{8}$$

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

The magnitudes of the correlation hole natural orbital occupation numbers for correlated wavefunctions provide a local measure of the importance of electron correlation in the wavefunction. In the case of an isolated pair of electrons the Fermi hole is equal to half of the total density (Eq. 4), in which case the Fermi hole natural orbital occupation numbers must equal half of the ordinary natural orbital occupations numbers, independently of the position of the probe electron.

5. THE FERMI HOLE MOBILITY FUNCTION

In an isotropic free electron gas the Fermi hole and the Coulomb hole follow the probe electron. That is, the shapes of these functions are constants with respect to the position of the probe electron. As the probe electron moves with respect to a fixed origin, the correlation holes move with it. In an isolated electron pair, however, the Fermi hole remains fixed with respect to the external potential (nuclear coordinates), and does not follow the motion of the probe electron. In the electronic wavefunction of a molecule, the Fermi hole exhibit an intermediate form of behavior.[20-23]

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. This behavior has been demonstrated in a movie[42] which presents the shape of the Fermi hole in the water molecule as a function of the position of the probe electron. This movie was produced by photographing contour maps of the Fermi holes determined by approximately 90 positions of the probe electron in a minimal basis SCF wavefunction for the water molecule.

The sensitivity of the Fermi hole to the position of the probe electron in a closed shell SCF wavefunction is measured by the Fermi hole mobility function,[22]

$$F(\vec{r}) = F_x(\vec{r}) + F_y(\vec{r}) + F_z(\vec{r}) \tag{9}$$

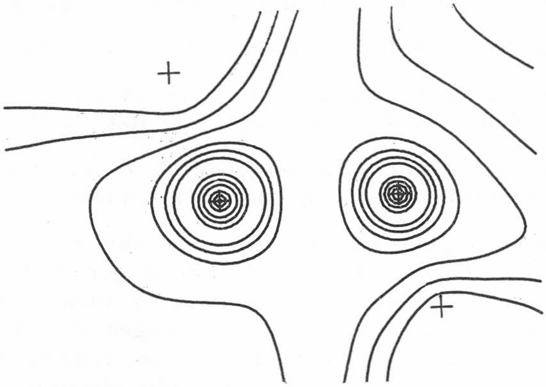

Figure 4. The Fermi hole mobility function for a double zeta SCF wavefunction for methanol. The contour levels indicate values of 0.1, 0.2, 0.4, 1.0, 2.0, 4.0, and 8.0 atomic units (bohr^{-2}). A methyl proton (upper left), the carbon nucleus (left of center), the oxygen nucleus (right of center), and the hydroxyl proton (lower right) are each indicated by a (+) mark.

where

$$F_v(\vec{r}) = \frac{2}{\varrho^2} \sum_{i>j} \left[g_i \frac{\partial g_j}{\partial_v} - g_j \frac{\partial g_i}{\partial_v} \right]^2 \tag{10}$$

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

$$F_0(\varrho) = (3\pi/4)(\varrho/2)^{2/3} \tag{11}$$

which provides an estimate of the Fermi hole mobility function in a uniform density electron gas.[22]

The Fermi hole mobility function $F(\vec{r})$ for methanol is shown in Figure 4. The difference between $F(\vec{r})$ and $F_0(\varrho)$ is shown in Figure 5. These figures are

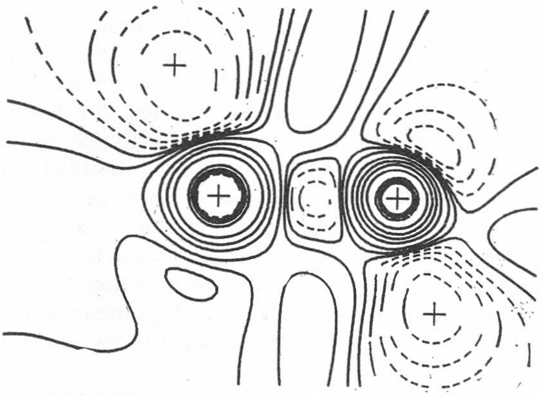

Figure 5. The difference between the Fermi hole mobility function and the Fermi hole mobility of a free electron gas with the same density. The solid lines indicate the same values defined in Figure 4. The broken lines indicate values of —0.1, —0.2, —0.4, and —1.0 atomic units (bohr^{-2}).

based on the same wavefunction used to determine Figures 1 to 3. Contour maps of $F(\vec{r})$ and $F(\vec{r}) - F_0(\varrho)$ for formaldehyde and ethane are shown in Figures 3, 4, 7, and 8 of Ref. 22. Contour maps of $F(\vec{r}) - F_0(\varrho)$ for a cyclic enone $C_4H_4O_2$ are shown in Figures 7 and 8 of Ref. 23. These figures show that $F(\vec{r})$ approaches a minimum at the position of each nucleus and $F(\vec{r})$ is less than $F_0(\varrho)$ in regions surrounding each of the nuclei.

In addition to the regions surrounding the nuclei, $F(\vec{r})$ is found to be less than $F_0(\varrho)$ in a region between the carbon and oxygen nuclei and in a region near the oxygen atom. The first of these may be identified with the C—O bond, while the latter is associated with the oxygen atom lone pair orbitals. When the probe electron is located in any of these regions the Fermi hole is relatively insensitive to the position of the probe electron and the shape of the Fermi hole resembles a conventional innershell orbital, lone pair orbital, or bonding molecular orbital. This is demonstrated by Figures 1, 2, and 3, which show Fermi holes associated with a C—H bond, a C—O bond, and an O—H bond, respectively.

The dependence of the shape and position of the Fermi hole on the position of the probe electron is entirely the result of interactions between pairs of electrons. If an electronic wavefunction could be described by isolated pairs of electrons, each occupying one of a set of nonoverlapping regions, then the Fermi hole mobility function would vanish everywhere, except at the boundaries between the regions. If the value of the Fermi hole mobility function is much less than $F_0(\varrho)$ in a certain region, then that region must be occupied by a relatively isolated pair of electrons. These regions are closely related to the loges proposed by Daudel[43-45]. Regions where $F(\vec{r}) > F_0(\varrho)$ resemble the boundaries between loges.

The relations between loges and the Fermi hole have been discussed by Bader and Stephens, who noted that the extent to which electrons may be localized in space is determined solely by the properties of the Fermi hole.[14] Indeed, when the probe electron is located in a region where $F(\vec{r})$ is less than $F_0(\varrho)$, the Fermi orbital is found to resemble a localized orbital determined by conventional methods.[41,46-54] Consequently, as is shown in the next section, the Fermi hole provides a simple and efficient method for transforming a set of canonical SCF molecular orbitals into a set of localized molecular orbitals.

The physical significance of the Fermi hole mobility function may be further illustrated by considering the case of two helium atoms labelled A and B and separated by a large distance along the x axis. Near nucleus A the Fermi hole mobility function is roughly proportional to ϱ_B/ϱ_A, where ϱ_A and ϱ_B are the density functions for each atom in the absence of the other. This ratio is extremely small because ϱ_B is much less than ϱ_A near nucleus A.

At the midpoint of the line segment joining the two nuclei $\varrho_A = \varrho_B$ and the Fermi hole mobility function has the value $F = -\varepsilon_1$, where ε_1 is the orbital energy for the helium atom 1*s* orbital. Consequently, the value of the Fermi hole mobility function at this position is equal to the height of the energy barrier which must be crossed in order for an electron to jump from one nucleus to the other.

6. LOCALIZED ORBITALS BASED ON THE FERMI HOLE

It has long been known that it is possible to transform the canonical SCF molecular orbitals of a molecule into a set of localized molecular orbitals by means of a unitary transformation. Each of these orbitals may usually be associated with a chemical bond, a lone pair atomic orbital, or an innershell atomic orbital. A number of methods for performing this transformation have been developed.[41,46–54] These methods depend on iterative sequences of unitary transformations based on appropriate combinations of integrals over the transformed molecular orbitals. These calculations may require a substantial computational effort beyond that required to calculate the canonical SCF molecular orbitals. In addition, these iterative methods converge very slowly for many molecules.

When the probe electron is located in a region where $F(\vec{r})$ is less than $F_0(\varrho)$ the Fermi orbital is found to resemble a localized orbital determined by conventional methods.[41,46–54] Consequently, Equation 8 provides a direct relationship between a set of canonical SCF orbitals $g_i(\vec{r})$ and a localized orbital $f_j(\vec{r}) = f(\vec{r}; \vec{r}_j)$, where $\vec{r}_j$ is a point in a region where $F(\vec{r}_j) < F_0(\varrho(\vec{r}_j))$. 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 $\vec{r}_j$, $j = 1$ to N, each of which is located in a region where $F(\vec{r}_j) < F_0(\varrho(\vec{r}_j))$. Ideally, each of these points should correspond to a minimum of $F(\vec{r})$ or $F(\vec{r}) - F_0(\varrho)$. 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 equation 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.[53,55] The resulting unitary transformation is given by

$$\mathbf{U} = (\mathbf{T}\,\mathbf{T}^{+})^{-1/2}\,\mathbf{T}, \tag{12}$$

where

$$T_{ij} = g_j(\vec{r}_i)/(\varrho(\vec{r}_i)/2)^{1/2}. \tag{13}$$

The transformation of a set of canonical SCF orbitals to a set of localized orbitals based on equations 12 and 13 has recently been demonstrated for each of three molecules.[56] 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, methylacetylene, is a molecule for which conventional methods have serious convergence problems.[57] 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 on the basis of 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 by 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.

In order to transform the eleven canonical SCF molecular orbitals of methylacetylene into a set of localized orbitals based on the Fermi hole, it is necessary to select four points in addition to the locations of the nuclei. One of these represents the C—C single bond, and three points are needed for the triple bond. The four C—H bonds are represented by points located on the protons. Transformation of the 22 SCF orbitals of the furenone, $C_4H_4O_2$, requires twelve points in addition to the ten nuclei. Boron trifluoride requires twelve points in addition to the locations of its four nuclei.

In each case the localized molecular orbitals determined by the Fermi hole were found to be very close to those determined by the orbital centroid criterion. For the furenone molecule, for example, 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. Likewise, the RMS off-diagonal overlap between the localized orbitals determined by the Fermi hole and those determined by the orbital centroid criterion for methylacetylene was found to be 0.012874.

7. CONCLUSIONS

The effects of the Pauli exclusion principle and electronic repulsion on the electronic wavefunctions of atoms molecules and solid state structures may be represented by the Fermi hole, the Coulomb hole, and composite correlation holes. Each of these may be described as a function of one electron which is parametrically dependent on the location of a second electron. This second electron is called the probe electron.

Each of the correlation holes possesses a natural representation determined by a set of correlation hole natural orbitals and their occupation numbers, each of which depends on the position of the probe electron. In the case of a wavefunction composed of a single Slater determinant the natural representation of the Fermi hole reduces to the square of a single orbital called a Fermi orbital.

Each molecule possesses regions in which the Fermi hole is relatively insensitive to the position of the probe electron. These regions are separated by regions in which the Fermi hole is more sensitive to the position of the probe electron. When the probe electron is located in a region where the Fermi hole is insensitive to the position of the probe electron, the Fermi hole resembles a localized molecular orbital.

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.

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SAŽETAK

Svojstva Fermijeve šupljine u molekulama

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Fermijeve šupljine u atomima, molekulama i čvrstom stanju posljedica su Paulijeva principa isključenja. Oblik Fermijeve šupljine određen je funkcijom koja ovisi o položaju probnog elektrona. Najjednostavniji opis te funkcije dobiva se s pomoću prirodnih orbitala Fermijeve šupljine i njihovih zaposjednuća. Ako je valna funkcija oblika Slaterove determinante, onda je Fermijeva šupljina dana kvadratom Fermijeve orbitale. S pomoću Fermijevih orbitala, kanonske SCF molekularne orbitale mogu se transformirati u lokalizirane orbitale koje su vrlo slične orbitalama dobivenim primjenom Boysova kriterija. Detaljno su razmotrene Fermijeve šupljine u metanolu.