

## Electron Delocalization and the Fermi Hole

Richard F. W. Bader,<sup>\*,†</sup> Andrew Streitwieser,<sup>\*,‡</sup> Arnst Neuhaus,<sup>‡</sup> Keith E. Laidig,<sup>‡</sup> and Peter Speers<sup>‡</sup>

Contribution from the Departments of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada, and the University of California, Berkeley, California 94720-1460

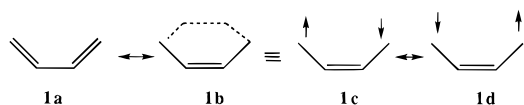
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**Abstract:** The delocalization of electrons is controlled by the Pauli exclusion principle through a corresponding delocalization of the density of the Fermi hole for electrons of given spin. It is proposed that the spatial distribution of the Fermi-hole density be used to provide a common, quantitative basis for the concept of electron delocalization, as it is used throughout chemistry. To this end, the following correspondences are made: The atomic patterns of delocalization of the Fermi hole recover the resonance structures corresponding to different possible spin-pairings and their relative importance, in terms of both energy and reactivity. The  $\pi$ -electron density of benzene distorted into a Kekulé-like structure is shown to be less delocalized than in the symmetrical structure. The effects of a hetero ring atom and of substituents on the delocalization of the  $\pi$ -electrons in benzene are quantified. To illustrate the range of phenomena that are determined by the delocalization of the Fermi-hole, it is shown that the measure of the extent of delocalization of the spin density from one hydrogen to another vicinal to it correlates with the variation in their spin–spin coupling with torsion angle, as predicted by the Karplus equation.

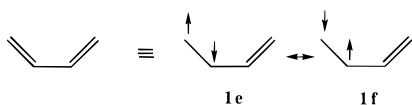
## Introduction

Electron delocalization is an important concept in modern organic chemistry. It is fundamental to both resonance theory and Hückel MO theory. The role of electron delocalization in the structure of benzene has been the subject of recent discussions.<sup>1,2</sup> Similarly, the role of delocalization in the acidity of carboxylic acids, long thought to be determining, has recently been receiving a re-evaluation.<sup>3–8</sup> One problem, of course, is that “delocalization” is not directly measurable and there is no single definition underlying the use of this concept throughout chemistry.

In his important book on resonance Wheland<sup>9</sup> summarized the use of a dotted line symbolism to represent delocalization in conjugated systems. The resonance structure **1b** for 1,3-butadiene is illustrative; it is a symbolic embodiment of the two structures **1c** and **1d** showing the coupling of electron spins without appreciable overlap. These symbols represent delocalization in butadiene within resonance theory.

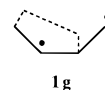


Even symbol **1a**, however, is a composite of two spin pairing structures, **1e** and **1f**.



There is therefore no qualitative difference between the two sets

of spin pairing; the two electrons in **1e** and **1f** have greater overlap and are more bonding than those of **1c** and **1d**. The difference is quantitative rather than qualitative but the quantitative difference is important and justifies the use of a different symbolism, a solid line rather than a dashed one. Structures **1e** and **1f** represent delocalization, 1,2-delocalization, relative to an electron “localized” on a single atom, but it is the type of delocalization not normally considered as such when chemists think about the 1,4-delocalization of conjugated systems. A third set of structures embodied in the symbol **1g** define 1,3-delocalization; this delocalization is expected to be much less important than 1,2- and 1,4-delocalization.



That is, we expect the relative contributions of the different delocalizations to be  $1,2 > 1,4 > 1,3$ .

It is the purpose of this paper to show that the spatial distribution of the Fermi hole, a consequence of the Pauli exclusion principle, provides a common basis for the quantitative representation of such resonance structures and of other concepts related to electron delocalization within molecular orbital theory.

**Determining the Delocalization of the Electron Density.**

To account for the indistinguishability of the electrons in the manner demanded by the Pauli principle, the wave function for a many-electron system must be antisymmetric with respect to the permutation of the space-spin coordinates for every pair of electrons. The result of this antisymmetry requirement on the *local position* of an electron is that no two electrons with the same spin can occupy the same point in space. The result on

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<sup>†</sup> McMaster University.

<sup>‡</sup> University of California, Berkeley.

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the spatial distribution of charge of an electron is described by the so-called Fermi hole. This is a distribution function for an electron of given spin, defined relative to an uncorrelated pair density, that determines the decrease in the probability of finding another electron with the same spin relative to a fixed position of the electron in question.<sup>10</sup> Thus, the Fermi hole describes the manner in which the charge of the reference electron is spread out in space, thereby excluding the presence of an identical amount of same-spin density. In other words, as an electron moves through space it carries with it a Fermi hole of ever changing shape, the density of the electron being spread out in the manner described by its Fermi hole. Accordingly, the extent of localization or delocalization of the density of the electron is determined by the corresponding localization or delocalization of its Fermi hole.<sup>11</sup> An expression for the density of the Fermi hole and a measure of its degree of spatial localization are readily obtained within the single-determinant Hartree–Fock formalism.<sup>11,12</sup> Luken and co-workers have employed these ideas in studies of the relation between the localization of the Fermi hole and the form of localized orbitals.<sup>13</sup> They also recast the discussion in terms of Fermi orbitals, the amplitudes of the Fermi hole, and the Fermi orbital mobility function, which describes the rate of change of the shape of the Fermi hole with respect to motion of the reference electron.<sup>14</sup>

The pair density  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  is a distribution function which, when multiplied by the infinitesimal volume elements  $d\mathbf{r}_1$  and  $d\mathbf{r}_2$ , determines the number of pairs formed between these two elements and integrates to the total number of distinct pairs,  $N(N-1)/2$ . The Fermi hole affects the pair distribution for parallel spin electrons. The expression for the pair density obtained from a single determinant wave function expressed in terms of spin orbitals  $\phi_i$  is

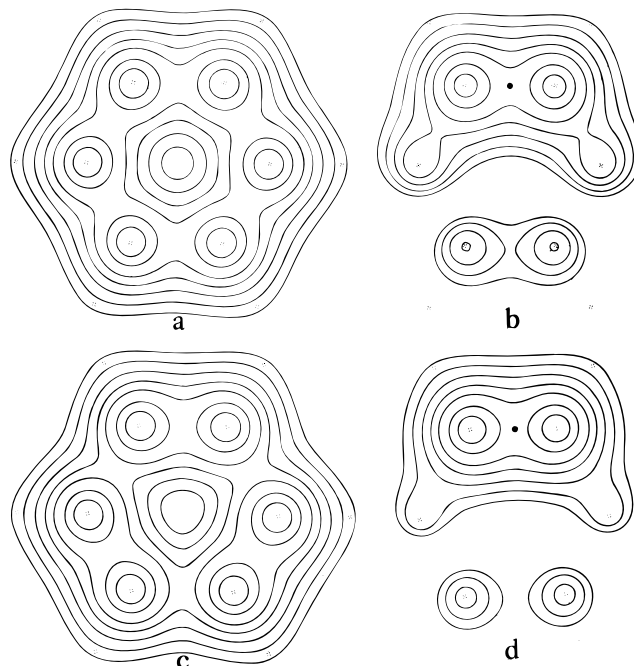
$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = (1/2) \sum_i \sum_j \{ \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_j(\mathbf{r}_2) - (\phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \phi_j^*(\mathbf{r}_2) \phi_i(\mathbf{r}_1)) \} \quad (1)$$

The first double sum corresponds to the product of number densities  $\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)$  and is the term that gives rise to the Coulomb repulsions in Hartree–Fock theory. The Coulomb term includes the self-repulsion of an electron in each orbital  $\phi_i$ , a result of the double sum integrating to  $N^2/2$  pairs rather than to the correct value of  $N(N-1)/2$ . The second double sum is the exchange term of Hartree–Fock theory. It is this term that corrects the product of number densities for the self-pairing of the  $N$  electrons and that, when integrated over  $e^2/r_{12}$ , corrects the Coulomb terms for the self-repulsion of each electron. It does this by removing the density equivalent to one electron as described by the Fermi hole.

The density of the Fermi hole for an  $\alpha$ -spin electron in Hartree–Fock theory, the quantity  $h^\alpha(\mathbf{r}_1, \mathbf{r}_2)$ , is obtained from the exchange density by dividing it by  $\rho^\alpha(\mathbf{r})$ , the density of  $\alpha$  spin electrons

$$h^\alpha(\mathbf{r}_1, \mathbf{r}_2) = \sum_i \sum_j \{ \phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \phi_j^*(\mathbf{r}_2) \phi_j(\mathbf{r}_1) \} / \rho^\alpha(\mathbf{r}_1) \quad (2)$$

where now the sums run over the  $\alpha$  spin orbitals. The



**Figure 1.** Contour maps of the  $\pi_\alpha$ -electron density and of its Fermi hole for the equilibrium geometry of benzene and for a distorted geometry as described in the text. The densities in this and the succeeding figures are plotted in a plane 0.5 au (0.26 Å) above the plane of the nuclei where the  $\pi$  density of benzene attains its maximum value. The contours denote the magnitude of the Fermi-hole density in all figures and increase in value from the outer one in the order  $5.0 \times 10^{-4}$ ,  $1.0 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $4 \times 10^{-3}$ ,  $8 \times 10^{-3}$ ,  $2 \times 10^{-2}$ , and  $4 \times 10^{-2}$  and are expressed in atomic units. The positions of the out-of-plane nuclei are indicated by open crosses. The position of a reference electron is denoted by a dot where the value of the Fermi-hole density in au is 0.011 in **b** and 0.015 in **d**.

expression for the density of the Fermi-hole given in eq 2 exhibits the following important limiting values: it equals  $-\rho^\alpha(\mathbf{r}_1)$  for  $\mathbf{r}_1 = \mathbf{r}_2$  corresponding to the complete removal of same-spin density from the position of the reference electron and it equals  $-1$  when integrated over the coordinates of the second electron corresponding to the removal of one electronic charge. The density of the Fermi hole given in eq 2 is unaffected by a unitary transformation of the orbital set and one obtains the same results whether the canonical or some localized set of orbitals is employed,<sup>11</sup> as is also true for the separate Coulomb and exchange contributions to the energy.

A plot of the density of the Fermi hole for a fixed position of the reference electron shows how the density for an electron with coordinate  $\mathbf{r}_1$  is spread out over space and whether it is localized or delocalized relative to a chosen boundary. The distribution of  $\pi$ -electrons of  $\alpha$  spin in benzene, 0.5 au above the plane of the ring where the  $\pi$ -density attains its maximum value, is shown in Figure 1a. Figure 1b is the Fermi-hole density for a reference electron positioned in this plane directly above the midpoint of a C–C bond. This picture is meant to make clear the distinction between the density arising from all of the electrons of given spin, as given by  $\rho^\alpha(\mathbf{r}) = (1/2)\rho(\mathbf{r})$ , and the local contribution to that density arising from the spreading out of the charge of one electron when positioned at some point in space, as determined by  $h^\alpha(\mathbf{r}_1, \mathbf{r}_2)$ . Figures 1c and 1d offer the same comparison of the total density and the single-electron delocalization contribution for benzene distorted into a Kekulé-like structure with alternating C–C bond lengths of 1.34 and 1.54 Å and representing an energy increase of 20 kcal mol<sup>-1</sup>. The Fermi density is seen to be more localized in this latter case.

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This figure illustrates another important property of the Fermi hole density: in general it exhibits maxima at positions removed from the position of the reference electron indicating preferred centers for the delocalized charge. Unlike Coulombic interactions or the other electrostatic interactions present in a system of electrons and nuclei, the exchange density does not decay in a monotonic manner with distance, but is able to transmit locally enhanced electrical effects to atoms removed from the position of the reference electron. For example, we shall find that the  $\pi$ -electrons on a carbon atom of benzene are preferentially delocalized onto the *para* as opposed to a *meta* carbon atom.

The degree to which some number of electrons are localized to a given spatial region is readily determined simply by calculating the fraction of the total possible Fermi correlation contained within the region.<sup>11,12</sup> The Fermi correlation for the  $\alpha$  electrons contained within a region  $\Omega$ , the quantity  $F^\alpha(\Omega, \Omega)$ , is obtained by the double integration over the region  $\Omega$  of the Fermi-hole density in eq 2, corresponding to every possible position of the reference electron within  $\Omega$ , weighted by the density of the reference electron. In Hartree-Fock theory,  $F^\alpha(\Omega, \Omega)$  is simply the sum of the squares of the overlap integrals of  $\alpha$  spin orbitals  $\phi_i$  and  $\phi_j$  over the region  $\Omega$ .

$$F^\alpha(\Omega, \Omega) = \int_{\Omega} d\mathbf{r}_1 \int_{\Omega} d\mathbf{r}_2 \rho^\alpha(\mathbf{r}_1) h^\alpha(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{ij} S_{ij}^2(\Omega) \quad (3)$$

If the Fermi hole for an electron is totally contained within  $\Omega$  for all positions within  $\Omega$ , then this double integral attains its limiting value of  $-N^\alpha(\Omega)$ , the spin population of the region  $\Omega$  obtained by integrating  $\rho^\alpha(\mathbf{r})$  over  $\Omega$ . This limiting value for  $F^\alpha(\Omega, \Omega)$  corresponds to the complete localization of the  $N^\alpha(\Omega)$  electrons within the region  $\Omega$ , there being no exchange with electrons in the remainder of the system. The ratio  $|F(\Omega, \Omega)/N(\Omega)|$  for electrons of either spin is thus the fraction of the total possible Fermi correlation per particle contained within a region  $\Omega$  and this ratio, when multiplied by 100, is  $f(\Omega)$ , the percent localization of the electrons in  $\Omega$ .

It is also possible to determine the extent to which the electrons in a region  $\Omega$  are delocalized into another region  $\Omega'$ , the quantity  $F^\alpha(\Omega, \Omega')$ . In analogy with the expression for  $F^\alpha(\Omega, \Omega)$ , this quantity is determined by the product of overlap integrals over both regions<sup>11,12</sup> (eq 4).

$$F^\alpha(\Omega, \Omega') = - \sum_{ij} S_{ij}(\Omega) S_{ij}(\Omega') \quad (4)$$

The quantity  $|F(\Omega, \Omega')|/N(\Omega)$  is the fraction of the Fermi correlation for the electrons in  $\Omega$  that is contained in  $\Omega'$  and it is, therefore, a measure of the extent to which the electrons in  $\Omega$  are delocalized over another region  $\Omega'$ . The quantity  $d(\Omega, \Omega') = |F(\Omega, \Omega')|/N(\Omega) \times 100$  is the percentage measure of this delocalization.<sup>11,12</sup> The method is given an atomic basis by identifying the regions  $\Omega$  with the basins of the topologically defined atoms in the theory of atoms in molecules.<sup>12</sup> The boundary enclosing an atomic basin is defined as one of local zero-flux in the gradient vector of the electron density. The calculation of the overlaps of orbital products over an atomic basin, the quantity  $S_{ij}(\Omega)$  that determines the Fermi correlation contained within one basin or its spreading into another, is accomplished using the program PROAIM.<sup>15</sup>

The delocalization function  $F(\Omega, \Omega')$ , since it measures the extent to which electrons are delocalized or shared over two atomic basins, provides a measure of bond order between  $\Omega$

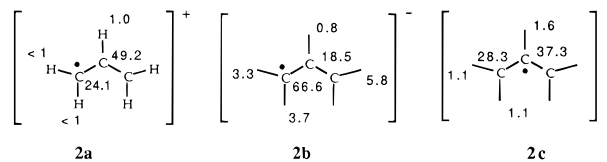
and  $\Omega'$ . Cioslowski and Mixon<sup>16</sup> and also Fulton<sup>17</sup> have used the products of the overlap integral  $S_{ij}(\Omega)$  to obtain definitions of bond order.

In systems possessing a plane of symmetry, the orbitals are classified as  $\sigma$  or  $\pi$ , depending on whether they are symmetric or antisymmetric with respect to reflection in the plane. Because of this property, the overlap integral  $S_{ij}(\Omega)$  vanishes when  $i$  and  $j$  refer to a member from each set. Consequently, both  $F(\Omega, \Omega)$  and  $F(\Omega, \Omega')$  are composed of separate and distinct contributions from the two sets of electrons and the localization or delocalization of the  $\pi$  electrons can be determined separately from that of the  $\sigma$  electrons in such systems.

## Results and Discussion

Wave functions were obtained using GAUSSIAN 92 and the 6-31++G\*\* basis set at the corresponding optimized geometries.<sup>18</sup> The Fermi-hole density and its integration were determined using an up-dated version of PROAIM.<sup>15</sup> Table 1 shows the values for  $N^\alpha(\Omega)$ , the  $\pi_\alpha$  spin population for atom  $\Omega$ , together with the values for  $f(\Omega) = |F(\Omega, \Omega)/N(\Omega)| \times 100$ , the percent localization of the density of the electrons on atom  $\Omega$  within the basin of  $\Omega$  and  $d(\Omega, \Omega') = |F(\Omega, \Omega')/N(\Omega)| \times 100$ , the percent delocalization of the density of the electrons in atom  $\Omega$  into the basin of atom  $\Omega'$ . In the neutral hydrocarbons,  $N^\alpha(\text{C})$  is slightly less than 0.5 because of the presence of a small amount of  $\pi$  density on adjacent hydrogens. The values of  $f(\Omega)$  and  $d(\Omega, \Omega')$  are summarized pictorially by structures given in the text, a dot denoting the atomic basin containing the reference electron.

**Acyclic Molecules.** In a molecule with a single  $\pi$  electron or a single  $\alpha, \beta$  pair, the density of the Fermi hole reduces to the density of the single  $\pi$  orbital for any position of the reference electron, as illustrated in Figure 2 for ethene and allyl cation. This follows since there is no other same-spin electron contributing density to any point in space to exclude the density of the reference electron. The percent localization is just the atomic spin population  $N^\alpha(\Omega)$  and the delocalization is the population of a neighboring atom. Thus the density of a  $\pi$  electron in ethene is equally delocalized 47% over each carbon while in allyl cation the localization/delocalization is 49% and 24% on the central and terminal atoms, respectively, (structure **2a**).



The exclusion effect takes hold in the allyl anion where there are two  $\pi$  electrons of each spin. The data in Table 1 show that not only do the terminal carbons have the majority of the  $\pi$  density but the density is also more localized on these atoms,  $f(\text{C}_1) = 67\%$ , than it is on the central atom, where  $f(\text{C}_2) = 37\%$  (structures **2b** and **2c**). The localization of the  $\pi$  density within the basin of a terminal carbon atom, as opposed to its delocalization into basins neighboring the central atom is illustrated in Figure 2. The distributions in Figure 2c and 2d

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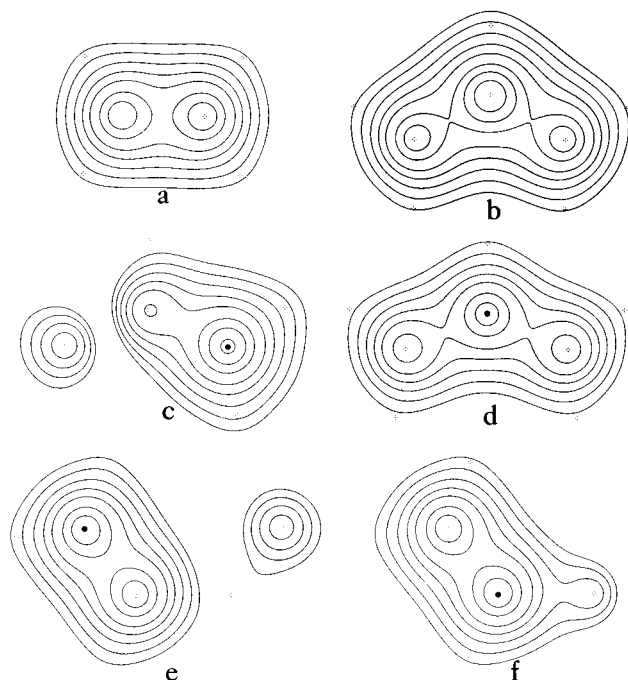
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**Table 1.** Total  $\pi$ -Density and  $\pi$ -Density Distribution

$\pi_\alpha^a$	molecule	ref atom	total $\pi_\alpha$ pop <sup>b</sup>	$-F(\Omega, \Omega')/N(\Omega) \times 100$ in the basin $\Omega$ of atoms																
				1	2	3	4	5	6	7	8	9	10							
1	C <sub>2</sub> H <sub>4</sub>	C <sub>1</sub>	0.4672	46.8	46.8															
1	C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	C <sub>1</sub>	0.2403	24.1	48.5	24.1														
		C <sub>2</sub>	0.4846	24.0	49.2	24.0														
1	C <sub>3</sub> H <sub>3</sub> <sup>+</sup>	C <sub>1</sub>	0.3293	32.9	32.9	32.9														
2	C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	C <sub>1</sub>	0.6897	66.6	18.5	5.8														
2		C <sub>2</sub>	0.4516	28.3	37.3	28.3														
2	C <sub>4</sub> H <sub>6</sub>	C <sub>1</sub>	0.4728	46.9	42.8	1.7	3.3													
		C <sub>2</sub>	0.4773	42.4	44.7	3.4	1.7													
3	C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	C <sub>1</sub>	0.5712	50.6	18.7	3.6	3.6	18.7												
3	C <sub>6</sub> H <sub>6</sub>	C <sub>1</sub>	0.4828	44.4	21.8	2.0	4.7	2.0	21.8											
	(S) C <sub>6</sub> H <sub>6</sub>	C <sub>1</sub>	0.4873	45.1	22.0	1.8	4.8	1.8	22.0											
	(U) C <sub>6</sub> H <sub>6</sub>	C <sub>1</sub>	0.4841	44.7	31.8 <sup>c</sup>	1.9	3.9	1.8	12.6											
3	C <sub>7</sub> H <sub>7</sub> <sup>+</sup>	C <sub>1</sub>	0.4170	39.2	23.1	3.0	2.9	2.9	3.0	23.1										
3	C <sub>5</sub> H <sub>5</sub> N	N <sub>1</sub>	0.7140	61.8	14.4	2.4	3.2	2.4	14.4											
		C <sub>2</sub>	0.3797	35.2	27.2	25.6	2.5	5.5	1.5											
		C <sub>3</sub>	0.4970	3.5	19.5	46.4	21.2	1.9	4.2											
		C <sub>4</sub>	0.4546	5.0	2.1	23.2	41.5	23.2	2.1											
4	C <sub>6</sub> H <sub>5</sub> CN <sup>d</sup>	N <sub>1</sub>	0.7207	71.3	25.5	0.9	0.8	0.1	0.5	0.1	0.8									
		C <sub>2</sub>	0.3183	57.7	27.9	9.4	1.9	0.2	0.7	0.2	1.9									
		C <sub>3</sub>	0.5230	1.3	5.7	46.6	18.7	1.8	3.9	1.8	18.7									
		C <sub>4</sub>	0.4660	1.2	1.3	21.0	42.6	22.8	2.1	4.7	1.8									
		C <sub>5</sub>	0.4807	0.1	0.1	2.0	22.1	44.5	21.6	1.9	4.5									
		C <sub>6</sub>	0.4663	0.7	0.5	4.4	2.1	22.3	42.8	22.3	2.1									
4	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> <sup>e</sup>	N <sub>1</sub>	0.9521	88.7	5.0	1.5	0.2	0.7	0.2	1.5										
		C <sub>2</sub>	0.4273	11.2	35.9	21.2	2.1	4.3	2.1	21.2										
		C <sub>3</sub>	0.5289	2.7	17.1	49.2	20.7	1.8	4.0	1.6										
		C <sub>4</sub>	0.4667	0.4	2.0	23.4	41.9	22.3	2.1	4.5										
		C <sub>5</sub>	0.5167	1.2	3.6	1.8	20.1	47.9	20.1	1.8										
5	C <sub>10</sub> H <sub>8</sub>	C <sub>1</sub>	0.4855	44.5	28.6	1.8	4.4	0.2	0.3	0.9	1.0	14.1	1.3							
		C <sub>2</sub>	0.4841	28.6	43.7	14.8	1.8	0.3	1.0	2.1	0.9	1.7	2.7							
		C <sub>9</sub> <sup>f</sup>	0.4924	13.9	1.7	4.8	1.3	1.3	4.8	1.7	13.9	42.5	17.0							

<sup>a</sup> Number of  $\pi$ -electrons with  $\alpha$ -spin. <sup>b</sup> Total population of  $\pi_\alpha$ -electrons. <sup>c</sup> The 1–2 bond is a short bond. <sup>d</sup> The cyano carbon is C2; the *ipso* carbon is C3, etc. <sup>e</sup> The *ipso* carbon is C2. <sup>f</sup> C9 is the bridge carbon bonded to C1, C8, and C10.

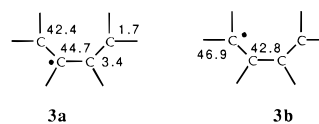


**Figure 2.** Contour maps of the Fermi-hole density: for the  $\pi_\alpha$ -electron in ethene in (a) and in allyl cation in (b) which are identical to their  $\pi_\alpha$ -density distributions; for two positions of the reference electron in allyl anion in (c) and (d) and in butadiene in (e) and (f). The values of the Fermi-hole density at the positions of the reference electron are 0.095 in c, 0.060 in d, 0.071, in e, 0.071 in f.

should be compared with Figure 2b showing the totally delocalized single  $\alpha$  electron in the cation, all maps integrating to one electronic charge. Figure 2c and the value for  $\rho(\text{C}_1)$

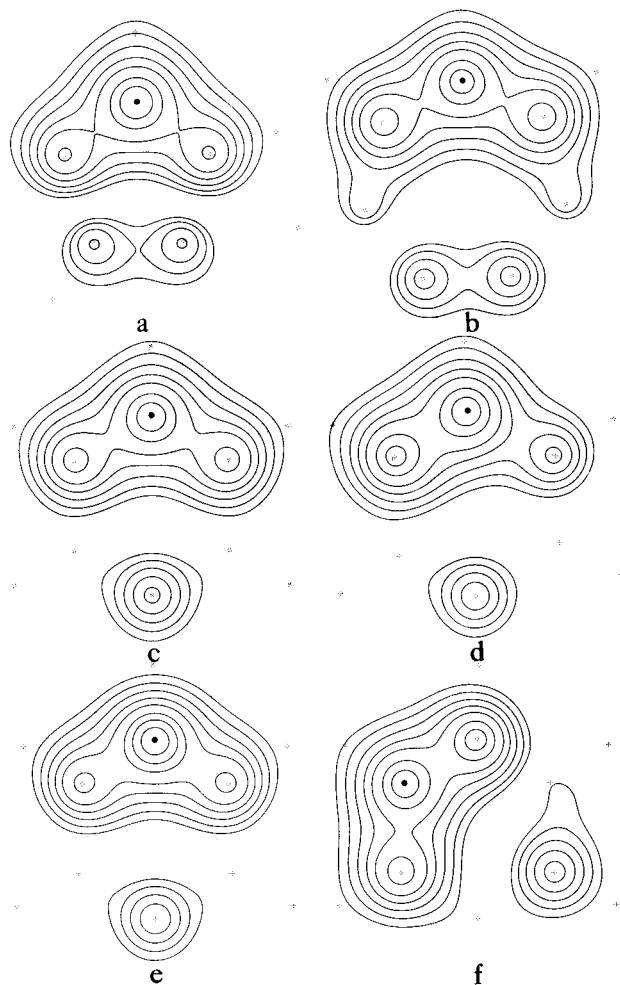
indicate the importance of the resonance structure having an electron pair localized on a terminal carbon, indicating that the preferred electrophilic attack at this point is a result of both the accumulation and pairing of the  $\pi$  density on this atom.

The butadiene molecule also has two doubly occupied  $\pi$  orbitals. The Fermi-hole distributions for a reference electron within the basin of a terminal and an interior carbon atom are shown in Figure 2. In both instances the  $\pi$  density is significantly delocalized only into the basin of the neighboring carbon to which it is formally linked by a double bond, structures **3a** and **3b**, with nearly 90% of the  $\pi$ -density localized within their basins, only slightly less than the value of 94% found in ethylene.



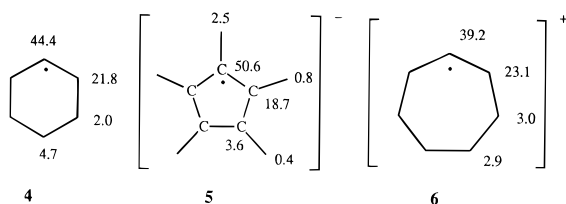
The plots of the density for the Fermi hole are similar to the plot of the  $\pi_\alpha$  density found in ethene, indicating that the delocalization of the  $\pi$  density outside the basins of the doubly bonded carbon atoms in this molecule is slight. The delocalization that is found corresponds, however, to the resonance structures **1b** and **1g** with the former, the structure associated with Diels–Alder addition, being the more important, as expected.

**Cyclic Molecules.** We next consider aromatic compounds in which delocalization is commonly regarded as more important. Figure 3 displays contour plots of the Fermi-hole density of the cyclopentadienyl anion, benzene, and the tropylium cation. The localization of the  $\pi$  electrons on a given carbon and their delocalization onto other atoms in the molecule are given in



**Figure 3.** Contour maps of the Fermi-hole density for the  $\pi_\alpha$ -electrons for indicated positions of the reference electron 0.5 au above the nuclear plane with the value of the density in au at the position of the reference electron given in brackets: (a) in cyclopentadienyl anion (0.080), (b) tropylium cation (0.061), (c) symmetrical benzene (0.071), (d) unsymmetrical benzene (0.071), and (e and f) pyridine with the reference electron above N (0.148) and above  $C_\alpha$  (0.067), respectively.

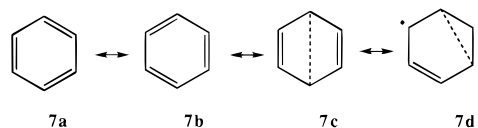
Table 1 and summarized in structures 4, 5, and 6.



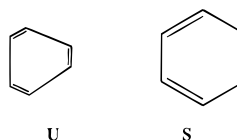
The extent of localization of the  $\pi$  electrons on a given carbon decreases with a decrease in the atomic spin population, being a maximum in the anion. In these symmetric cyclic molecules there is significant delocalization over both neighboring atoms, an effect that increases with ring size and, as a consequence, the electrons are more delocalized in these molecules than they are in the acyclic ones considered above, a point made evident by a comparison of Figures 2 and 3. The delocalization of  $\pi$  density in the tropylium cation is somewhat greater than it is in benzene, a result of the greater spatial extent available in the seven-membered ring.

In the odd-membered rings, the interatomic delocalization of the electrons on a given atom decreases with the distance of the second atom from the one in question (Table 1). In benzene, however, there is significantly greater delocalization of the  $\pi$

density into the basins of the *para* as compared to the *meta* carbons. In correspondence to resonance structures, the data in Table 1 show that the Kekulé structures **7a** and **7b** are of principal importance, the Dewar structures, such as **7c**, less so, and structures of the type **7d** of still less importance.



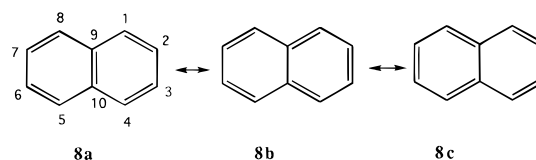
The effect of geometrical distortions on the delocalization of the  $\pi$  electrons in benzene was studied by considering a symmetrical distortion (**S**) in which each equilibrium C—C bond length of 1.42 Å was increased by 0.06 Å in an  $A_1$  stretching mode and an unsymmetrical one (**U**) obtained by alternately increasing and decreasing the bond lengths to 1.54 and 1.34 Å, respectively.



The effect of such a distortion on the density of the Fermi hole for the reference electron positioned above the midpoint of a C—C bond was illustrated in Figure 1, while Figure 3 makes the same comparison for the reference electron placed above a carbon nucleus. There is no significant change in the delocalization of the  $\pi$  electrons for a symmetrical distortion of the ring (Table 1). The data show that the same is not true for an unsymmetrical displacement. Figures 1d and 3d show that the Fermi-hole density for the **U** structure resembles the  $\pi_\alpha$  density of an isolated ethylenic bond, Figure 2a, for both extremes in the position of the reference electron relative to the nuclei of a shortened bond. The extent to which the two distributions are the same determines the extent to which the density of no other  $\alpha$  or  $\beta$  electron can enter the basins of the carbons of the shortened bond.

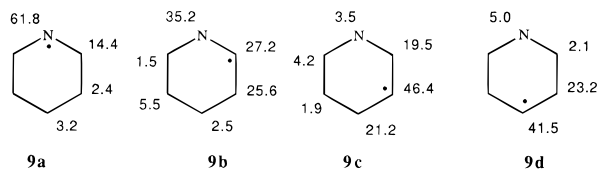
The data given in Table 1 for naphthalene indicate that the fusing of a second ring onto benzene changes the pattern of its electron delocalization. The  $\pi$  density on C1 delocalizes preferably into the basin of atom C2 rather than into the neighboring bridging atom C9 and the pattern of the Fermi-hole density exhibits similarity to the localized distribution found for butadiene. The atom C2 exhibits the same unsymmetrical behavior with respect to its neighbors, its  $\pi$  density delocalizing to a greater extent into C1 than C3. Thus, nearly 72% of the  $\pi$  density for the C1—C2 group is localized within the group.

Each bridging carbon atom is linked to three neighbors and its  $\pi$  density is more delocalized than is that for the ring carbons with the second bridging atom being the major recipient of the delocalized density. These results show that of the resonance structures for naphthalene, **8a** is more important than **8b** or **8c**.



**Effect of Hetero Atom Substitution on Aromatic Delocalization.** We next investigate the question of what happens to the delocalization of the  $\pi$  density if one substitutes one carbon atom of the benzene ring with a more electronegative

nitrogen atom. The spatial distribution of the  $\pi$  density and its Fermi hole in pyridine are strongly affected by the nitrogen atom. Nearly 62% of this density remains localized within its basin and only 38% is delocalized, compared to 56% delocalization for a carbon in benzene (Figure 3e and structure **9a**).



The electronegativity of nitrogen also strongly affects the delocalization of the  $\pi$  density of a neighboring carbon atom, the  $\pi$  density on  $C_\alpha$  being more delocalized onto the nitrogen atom than it is localized within its own basin, 35% compared to 27% (Figure 3f and structure **9b**). This results in a correspondingly perturbed version of the Fermi-hole density for a carbon in benzene, including a delocalization tail on the *para* atom. The presence of the nitrogen atom enhances slightly the localization of the density at a  $C_\beta$  atom compared to benzene and the Fermi-hole distribution is similar to that for a carbon in benzene itself, **9c**. However, the effect of the nitrogen is again significant for  $C_\gamma$ , **9d**, enhancing the delocalization of its  $\pi$  density onto the neighboring carbons and the nitrogen in the *para* position, relative to a carbon in benzene.

The comparison of the localization of the Fermi-hole density for the cyclic with those for the acyclic molecules demonstrates that the  $\pi$  density is delocalized to a significantly greater extent in the former systems and that this delocalization is characteristic of so-called aromatic molecules. The presence of an electronegative atom in pyridine reduces the extent of the delocalization of the  $\pi$  density out of the basin of the hetero atom itself, but increases the delocalization found for the  $C_\alpha$  and  $C_\beta$  atoms.

**Substituent Effect on Aromatic Delocalization.** The interaction of a substituent having its own  $\pi$  system with the  $\pi$  system of benzene is investigated by determining the manner and extent of delocalization of the  $\pi$  system of the cyano group into the phenyl system (Table 1). One sees that 71% of the 0.72  $\pi_\alpha$  electrons on nitrogen are localized within their own basin and 97% within the CN group, leaving only 2.3% to be delocalized over the phenyl group. The situation is less severe for the carbon of CN where 14% of its  $\pi$  density is delocalized into the phenyl group, mostly onto the *ipso* carbon, compared to 58% delocalization onto nitrogen. As with a  $C_\alpha$  in pyridine, the  $\pi$  density on carbon of CN is more delocalized onto nitrogen than it is localized within its own basin. The  $\pi$  populations of the *ipso* and *meta* carbons are increased relative to the remaining positions within the ring. The  $\pi$  density of the *ipso* carbon is more localized at 47% than it is for a carbon in benzene. The behavior of the *meta* carbon is similar to that found in benzene itself. The major effect of the cyano group is to decrease the degree of delocalization of the  $\pi$  density to the *ortho* and *para* carbon atoms relative to benzene itself, the same atoms that undergo a reduction in their  $\pi$ -populations (Table 1).

In planar aniline a nitrogen atom with a lone pair of electrons interacts with the  $\pi$  system of the phenyl group. The population of  $\pi_\alpha$  electrons on nitrogen is 0.95 and the presence of this atom reduces the corresponding populations of the *ipso* and *meta* carbons while increasing that of the *ortho* and *para* atoms. The density of the lone pair on nitrogen is relatively localized with only 9% of its  $\pi$  density being delocalized over the carbons of the phenyl group, primarily onto the *ipso* carbon. The major effect of the amino group is to significantly increase the degree of localization of  $\pi$  density at the positions of the *ortho* and

*para* carbon atoms, to 49% and 48%, respectively, compared to benzene itself.

Thus, groups that are activating or deactivating in electrophilic substitution reactions exert opposite effects on the delocalization of the  $\pi$  density in a phenyl group, as well as on its distribution relative to that found in benzene. A deactivating group, such as cyano, decreases both the  $\pi$  population and its degree of localization at the *ortho* and *para* carbons, leaving the *meta* carbon nearly unperturbed, while an activating group, such as amino, has the opposite effect of increasing the  $\pi$  population and its localization on the *ortho* and *para* carbons and, in addition, decreasing the population and localization of the  $\pi$  density on the *meta* carbon.

The maxima in the negative of the Laplacian of the electron density determine the sites where electronic charge is concentrated. These charge concentrations are found to correlate with the number and relative positions of the localized electron pairs assumed in the Lewis model, as employed in the VSEPR model of molecular geometry.<sup>12,19</sup> The maxima also determine the sites of electrophilic attack in accordance with their identification as Lewis bases. The pattern of localization of the phenyl  $\pi$  density resulting from the presence of an activating or deactivating group, as determined by the localization of the Fermi-hole density, is identical to the perturbations that the same groups cause in the Laplacian of the total electron density of the phenyl group. A deactivating group decreases the degree of charge concentration at the *ortho* and *para* positions, leaving the *meta* value unchanged, while an activating group increases the extent of charge concentration at the *ortho* and *para* positions and decreases it at the *meta* positions.<sup>20</sup> Thus, the localization of charge concentrations of the Laplacian distribution mirror the localization of the Fermi-hole density, as found here and as previously demonstrated,<sup>21</sup> and the topology of the Laplacian of the electron density is a reflection of the properties of the pair density.

**Delocalization of the Fermi Hole and Spin-Spin Coupling Constants.** Karplus<sup>22a</sup> used valence bond arguments to obtain an empirical expression for the coupling of the spins of vicinal protons connected by a C-C bond. The coupling of proton spins is dominated by the Fermi contact term, as a result of the nuclear spins polarizing the spin density in their immediate vicinity. McConnell<sup>23</sup> has shown, using Hartree-Fock theory, that this term is proportional to the difference in two pair probabilities,  $P^{\alpha\beta}(N,N') - P^{\alpha\alpha}(N,N')$ . The first term represents the probability of simultaneously finding an electron of  $\alpha$  spin at nucleus N and one of  $\beta$  spin at nucleus N', while the second term represents the corresponding probability for two electrons of  $\alpha$  spin. In words, the coupling is proportional to the excess in the density of a  $\beta$  spin at nucleus N' when an electron of  $\alpha$  spin is at N. For a single-determinant wave function, the excess  $\beta$  spin at N' is proportional to the  $\alpha$ -spin density removed by the Fermi hole at N' for an  $\alpha$  reference electron placed at nucleus N. That is, the coupling is proportional to the Fermi-hole density  $h^\alpha(N,N')$ . This follows since the motions of electrons of opposite spin are uncorrelated in Hartree-Fock theory and  $P^{\alpha\beta}(N,N')$  reduces to just the product of the two spin densities at the two nuclei, that is,  $P^{\alpha\beta}(N,N') = \rho^\alpha(N)\rho^\beta(N')$ , while  $P^{\alpha\alpha}$ -

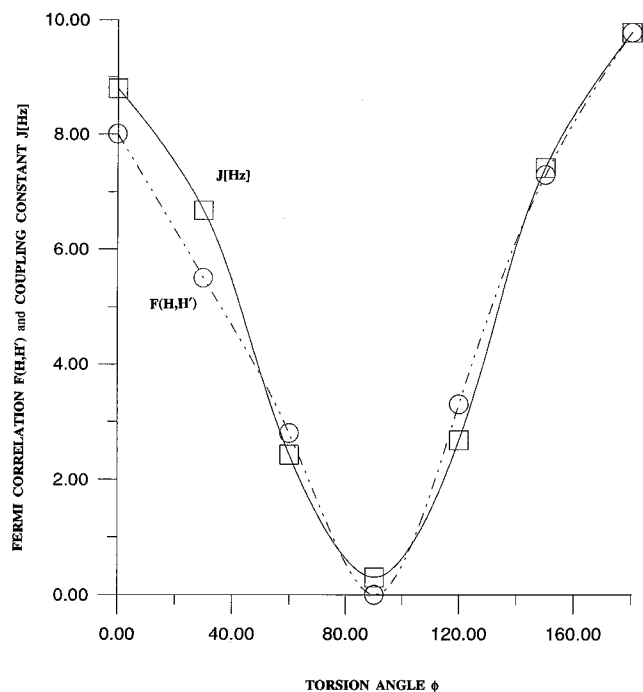
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**Figure 4.** Karplus plot of spin–spin coupling for vicinal protons versus torsion angle, overlaid with suitably scaled values of  $F(\text{H,H}')$ , the quantities that determine the extent of delocalization of the density of  $\alpha$ -spins on H into the basin of  $\text{H}'$ , as a function of torsion angle.

$(\text{N,N}')$  is modified by the density of the Fermi hole and is given by  $\rho^\alpha(\text{N})\rho^\alpha(\text{N}') + \rho^\alpha(\text{N})h^\alpha(\text{N,N}')$ .

Consequently, the delocalization of the Fermi-hole density from one proton onto another should parallel the magnitude of their spin–spin coupling. This is borne out by the excellent correlation found between the coupling of vicinal protons as a function of torsion angle obtained using the simple  $\cos^2 \phi$  form of the Karplus equation<sup>22b</sup> and the corresponding measure  $F(\text{H,H}')$  of the delocalization of the Fermi-hole density between vicinal hydrogens illustrated in Figure 4. The Fermi correlation  $F(\text{H,H}')$  was determined for the total density of  $\alpha$ -spins in the ethane molecule for a range of torsion angles.

## Conclusions

This paper has presented examples to establish the validity of a formalism for quantitatively assessing the delocalization of electrons in terms of the delocalization properties of the Fermi-hole density, a formalism that can be applied to any level of approximation to the wave function.<sup>11</sup> Localization of the Fermi-hole density for an electron of given spin leads to the formation of a localized pair. Its delocalization onto two centers implies a pairing of the electrons between them. This coupling can involve atoms once, twice, or farther removed from the

position of the reference electron. Thus, substituents in systems with delocalized electron distributions affect the pair density as well as the density itself at sites well removed from the site of substitution, as illustrated here for the phenyl group. Resonance structures used to represent the principal spin pairing structures of valence bond theory can be placed in one-to-one correspondence with the principal patterns of the delocalization of the Fermi-hole density that determine the location and degree of pairing. The  $\pi$  density of an aromatic system is shown to be significantly delocalized over a number of atomic centers and in a manner consistent with the energy ordering of the principal resonance structures.

It is important to emphasize that all physical measures of electron localization are determined by the localization of the Fermi-hole density, including ELF, the electron localization function recently proposed by Becke and Edgecombe.<sup>24</sup> ELF is based upon the function  $\Delta$  introduced by Tal and Bader,<sup>25</sup> a measure of the difference between the positive definite form of the kinetic energy density,  $G(\mathbf{r}) = (\hbar^2/2m)\sum_i |\nabla\phi_i|^2$ , and its limiting form,  $g(\mathbf{r}) = (\hbar^2/8m)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})$ , for a single electron or a two-electron Hartree–Fock ground state,  $g(\mathbf{r})$  equaling  $G(\mathbf{r})$  at positions coincident with and far removed from nuclei. Tal and Bader showed that  $\Delta \geq 0$  and that the condition for  $\Delta$  vanishing is that each orbital be completely localized to a *separate* region of space, pointing out that since this is the same condition that maximizes the localization of the Fermi hole, eq 3, the vanishing of  $\Delta$  implies the spatial pairing of electrons.<sup>25</sup> Becke and Edgecombe<sup>24</sup> were led to the use of  $\Delta$  in ELF because it is the leading term in the Taylor expansion of the conditional pair probability,  $\rho^\alpha(\mathbf{r}_2) + h^\alpha(\mathbf{r}_1, \mathbf{r}_2)$ , when spherically averaged. This term and  $\Delta$  vanish when the Fermi hole is maximally localized to yield a spatially localized pair of electrons in a closed-shell system.

Relating the concept of electron delocalization to its physical cause as embodied in Pauli's exclusion principle provides a common basis for the discussion and determination of its effect on the many properties that are directly or indirectly determined by this phenomenon, from energetic stability, to substituent directing effects, and to the understanding of spin–spin coupling constants.

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