J. Phys. Chem. A **2006,** *110,* 12191−12203

Comparison of the Localization of an Electron As Determined by the Two-Particle Distribution Function and by the Single-Particle Sharing Index

Robert L. Fulton[†]

Department of Chemistry and Biochemistry, The Florida State University, Tallahassee, Florida 32306

Received: May 30, 2006; In Final Form: August 31, 2006

A comparison of the measure of the delocalization of a particle based on the two-particle distribution function and that based on the single-particle density matrix is made using a simple set of wave functions which span states ranging from single determinant ground and doubly excited states through states mimicking correlated states and which include the singly excited state for electrons and for bosons replacing electrons in H_2. The comparison further includes an analysis of the application of the measures to a classical ideal gas and a compressible fluid. It is found that the values of the integrated atom−atom measures agree for a range of wave functions involving combinations of the two single determinant (and equivalent Bose) wave functions but disagree for a different range of these wave functions and for the singly excited wave functions. Aside from the single determinant (and equivalent Bose) wave functions, the two sets of point−point measures that underlie the integrated measures all differ. For the sets of wave functions considered, the values of the measures are identical for electrons and bosons. When applied to a closed classical ideal gas and to a closed compressible fluid, the delocalization measure based on the two-particle distribution has a residual long range term, whereas the sharing index in the classical limit gives a completely localized particle. In general, the two measures describe different aspects of the behavior of the particles. The measures based on the two-particle distribution function give only two-particle properties and the single-particle density, and the sharing quantities give only single-particle properties. The latter includes, however, the quantitative measures of the delocalization of a single particle, the point−point sharing index and the sharing amplitude.

I. Introduction

There is a common conception that in a many-electron system the two-particle distribution function can be used to determine the extent of delocalization of a single electron.[1−11] The argument is essentially the following.[12] Because the wave function for a collection of fermions is antisymmetric with respect to the pairwise interchange of electron coordinates (spatial plus spin), the probability that two electrons will be found at the same spatial point with the same value of the spin variable is zero. Choose one of the electrons in the two-particle distribution function as the reference electron e*. In general, the probability that a second electron with the same spin as the first will be in the immediate vicinity of the first e* is diminished from the product of the single-particle (same spin) probabilities at the two points. This diminution of probability is taken to be a measure of the delocalization of the first electron at the position of the second electron, and hence a measure of the "Fermi hole".

This "Fermi hole" has been interpreted by Bader[7] as providing "a description of how the density of an electron of given spin, called the reference electron, is spread out from any given point into the space of another same spin electron, thereby excluding the presence of an identical amount of same-spin electron."[13] In turn Bader[3] has used this interpretation of the behavior of the two-particle distribution function as the basis for the definitions of a localization index $\lambda(\mathrm{A})$ and a delocalization index $\delta(\mathrm{A,B})$ where A and B refer to two volumes. The former is called a measure of the total Fermi correlation within a volume V_A and the latter is called a measure of the extent to which the Fermi density of the reference electron e* in volume V_A is spread into volume V_B. Fradera[6] is more specific regarding the meanings of the indices: $\lambda(\mathrm{A})$ is the number of electrons localized in V_A and $\delta(\mathrm{A,B})$ is the number of electrons delocalized between the two volumes V_A and V_B.

The beginnings of this interpretation can be traced to the 1934 paper by Wigner and Seitz[14] in which the terms "Fermi hole" and "correlation hole" were introduced. In that paper, the Fermi hole was described as "... the hole in an otherwise uniform electron fluid around every electron because the probability of two electrons having parallel spin being very near is very small." The correlation hole was characterized as "arising from the mutual repulsion terms, but they lie beyond the scope of Fock's equations." For single determinant wave functions, the Fermi hole is the result of the antisymmetry of a wave function with respect to electron interchange while the correlation hole vanishes for antiparallel spins. The latter is therefore determined by correlations beyond those embodied in Hartree−Fock wave functions and therefore beyond those resulting from the Pauli principle. The shape of the Fermi hole in a uniform electron fluid was given in an earlier paper of Wigner and Seitz.[15] It is to be noted, however, that in connection with the terms "Fermi hole" and "correlation hole" Wigner and Seitz restricted their remarks to the behavior of the two-particle distribution function in "an otherwise uniform electron fluid", with no reference to a delocalization of an electron. Slater, in his review[16] in 1934 and in a later paper[17] in 1951, Maslen[18] in his 1958 paper on the shapes of Fermi holes in atoms, and McWeeny in his review[19] in 1960, also restricted their remarks to the behavior

---

[†] E-mail: fulton@chem.fsu.edu.

10.1021/jp0633401 CCC: $33.50

of the two-particle distribution function and/or to the exchange hole associated with the distribution function, again with no reference to the delocalization of an electron. Ruedenberg[20] in 1962 seems to have been the first to have made a subtle change in the interpretation of the Fermi hole from what McWeeny called a “correlation factor”, related to the two-particle distribution function in a classical manner, to the sharing (or delocalization) of a single electron between points, calling the negative of the correlation factor the “sharing fraction”.

The analysis considered above initially raises two concerns. The first is the role of the Pauli principle in determining the extent of delocalization of the reference electron, the second is the role of the two-particle distribution function in determining single-particle properties. Consider the following two questions: “What is the role of the Fermi hole in determining the delocalization of an electron?”, and “What single particle properties can be deduced solely from the knowledge of the two-particle distribution function?”

At the outset let the two-particle distribution function (normalized to 2) for the two electrons in H_2 be given by $\rho^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ and the corresponding single-particle density be given by $\rho^{(1)}(\mathbf{r}\sigma)$ where $(\mathbf{r}\sigma)$ stands for the space coordinates $\mathbf{r}$ and a discrete index σ which, in the case of an electron, is a spin index.

Consider the hydrogen molecule in its ground electronic state and constrained to be at the center of an evacuated container, which is large compared to the size of H_2. Electrons with the same spin as one of the pair of electrons in the molecule are constrained to be in the walls of the container because the specification of a singlet state demands that within the molecule the same spin distribution function vanish, $\rho^{(2)}(\mathbf{r}_1\sigma,\mathbf{r}_2\sigma) = 0$. Let the reference electron with coordinates given by $(\mathbf{r}^*\sigma^*)$ be denoted by e*. According to the prescription given above, the Fermi hole due to e* is described by

$$\rho^{(2)}(\mathbf{r}\sigma^*,\mathbf{r}^*\sigma^*) - \rho^{(1)}(\mathbf{r}\sigma^*)\,\rho^{(1)}(\mathbf{r}^*\sigma^*) = -\rho^{(1)}(\mathbf{r}\sigma^*)\,\rho^{(1)}(\mathbf{r}^*\sigma^*)$$

the diminution of $\rho^{(2)}(\mathbf{r}\sigma^*,\mathbf{r}^*\sigma^*)$ from the product of the one-particle density being complete. As a result, the Fermi hole for e* extends over the region of the interior of the container where $\rho^{(1)}(\mathbf{r}\sigma^*)$ is nonvanishing. Now the reason for the vanishing of $\rho^{(2)}(\mathbf{r}\sigma^*,\mathbf{r}^*\sigma^*)$ is not the Pauli principle; rather it follows from the fact that there are but two electrons in the singlet state and from the location of the molecule relative to the container walls. This is but one, perhaps extreme, example that there are reasons other than the Pauli principle that influence the behavior of the two-particle distribution function.

Second, suppose that we are given only the two-particle distribution function for a system of N particles

$$\rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$$

The normalization of this distribution function, when integrated and summed over all coordinates, is to $N(N - 1)$. The integral over the coordinates $(\mathbf{r}_2\sigma_2)$ gives

$$(N - 1)\rho_N^{(1)}(\mathbf{r}_1\sigma_1)$$

where $\rho_N^{(1)}(\mathbf{r}_1\sigma_1)$ is the single-particle density at $\mathbf{r}_1$ with spin σ_1 in the N electron system. In the absence of any further information, this is the only single-particle property inherent in the two-particle distribution function. If we are now told that the particles are fermions, we know, as a result of the Pauli principle, that the two-particle distribution function vanishes when $(\mathbf{r}_1\sigma_1)$ equals $(\mathbf{r}_2\sigma_2)$. The converse, that the vanishing of the two-particle distribution function when $(\mathbf{r}_1\sigma_1)$ equals $(\mathbf{r}_2\sigma_2)$ implies the Pauli principle, need not hold. The connection to the single-particle density still holds, but there is no other information about the behavior of a single particle inherent in the two-particle distribution function. In particular, the two-particle distribution function in general does not contain information about the delocalization of an electron, nor does it necessarily reflect the spreading of the electron density of a single reference electron at a point into neighboring regions of space as has been suggested by others.[1−11] To obtain further information about the behavior of a single electron requires knowledge of some property governing the wave function, e.g., that the wave function be expressible as a single determinant.

Now the average value of any single-particle property can be found from the single-particle density matrix, with the implication that all single-particle properties can be found from the single-particle density matrix. In particular, the delocalization (or spread) of a single particle should be obtainable from the single-particle density matrix—no knowledge of the two-particle distribution should be necessary for the determination of the extent of delocalization of an electron.

The implementation of this observation leads to a different measure of the delocalization of an electron in a many-electron system, a measure given solely by single-particle quantities. These are the sharing amplitude $\langle\zeta;\zeta'\rangle$, which is intimately connected to the single-particle density matrix, and the sharing index $I(\zeta;\zeta') \equiv |\langle\zeta;\zeta'\rangle|^2$.[21] ζ and ζ' stand for the spatial plus spin coordinates $(\mathbf{r}\sigma)$ and $(\mathbf{r}'\sigma')$. By integrating the arguments ζ and ζ' of $I(\zeta;\zeta')$ over the volumes V_A and V_B, respectively, we obtain indices which in some cases have numerical values similar to $\lambda(A)$ and $\delta(A,B)$. We denote the indices so found from the sharing indices as I_{AA} and $B_{AB} \equiv 2I_{AB}$. When the many-particle wave function is a single determinant wave function, the numerical values of $\lambda(A)$ and $\delta(A,B)$ are identical to those of I_{AA} and B_{AB}. Wang and Werstiuk attempted to derive I_{AA} and B_{AB} from the expressions for $\lambda(A)$ and $\delta(A,B)$ when electron correlation is included.[8,22] However, comparison of $\lambda(A)$ and $\delta(A,B)$ with I_{AA} and B_{AB} showed systematic differences, the differences tending to increase as the covalency increases. Although the differences for the states of the molecules considered by Wang and Werstiuk do tend to be small, the differences are nonzero. These differences persist in the compilations given in a recent review of electron delocalization in aromatic molecules.[11] Wang and Werstiuk indicate that “The differences between our results and the F-A-B results[3] may derive from a difference in the qualities of the densities used in the two studies.” This raises the question as to why such differences exist. If the differences in the values of the indices are not due to the difference in the qualities of the densities, the differences must be intrinsic to the indices themselves. It is our contention that this latter is the case—the connection between the two-particle distribution function and the delocalization of a single electron holds neither for general wave functions nor for general density matrixes. The agreement of the values of the two-particle indices $\lambda(A)$ and $\delta(A,B)$ with the single-particle sharing indices I_{AA} and B_{AB} holds fortuitously for single determinant wave functions. In this paper we show that, in general, the two sets of indices are intrinsically different. They in fact measure different aspects of the behavior of electrons in a many-electron system.

One premise in the following is that any measure of the delocalization of an electron (or, in general, any particle including bosons) should be valid for any wave function and by inference for any state of the electrons, be it the ground electronic state, some excited electronic state, some state which is not an energy eigenstate, a general mixed (impure) state, or in the classical limit.

In the next section we give brief reviews of the two-particle distribution function and of the sharing quantities as used in attempts to determine the delocalization of an electron. This is followed by a section in which the delocalization measures obtained from the two-particle distribution function are compared to the corresponding sharing indices for some simple fermionic and bosonic wave functions describing the ground and excited states of (pseudo) H_2. The penultimate section applies these measures to two classical systems, an ideal gas mixture and a single component compressible liquid. In both cases we find that the measures based on the two-particle distribution function indicate that there is long ranged delocalization of the classical particles for which there is no Fermi hole. In contrast, the sharing quantities give complete localization of the particles in the classical limit. The final section summarizes our results.

II. General Considerations

Consider a system of N particles. Let the position and spin (or other degree of freedom which for convenience we call spin) variables of particle i be denoted by $\mathbf{r}_i$ and σ_i. The two-particle distribution function [normalized to $N(N-1)$ when integrated over the spatial variables and summed over the spin variables] is here denoted by $\rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$.[23] The particle density at the point $(\mathbf{r}_1\sigma_1)$, denoted by $\rho_N^{(1)}(\mathbf{r}_1\sigma_1)$ and normalized to N, is related to the two-particle distribution function by

$$(N-1)\rho_N^{(1)}(\mathbf{r}_1\sigma_1) = \sum_{\sigma_2}\int d\mathbf{r}_2\, \rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) \qquad (1)$$

The average number density irrespective of spin is

$$\rho_N^{(1)}(\mathbf{r}_1) = \sum_{\sigma_1}\rho_N^{(1)}(\mathbf{r}_1\sigma_1)$$

and average number $N_N(\sigma_1)$ of electrons having spin σ_1 is

$$(N-1)N_N(\sigma_1) = \sum_{\sigma_2}\int d\mathbf{r}_1 \int d\mathbf{r}_2\, \rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) \qquad (2)$$

A subsequent sum over σ_1 gives $N(N-1)$. It should be noted that these sum rules have nothing to do with the nature of the particles; they hold whether the particles be fermions, bosons, or classical particles. As a consequence, the sum rules have nothing to do with the existence or nonexistence of a Fermi hole.

It is well-known that, as a result of the antisymmetry of a wave function describing fermions, the two-particle distribution function vanishes when the particles are electrons and the two sets of coordinates are equal, $(\mathbf{r}_1\sigma_1) = (\mathbf{r}_2\sigma_2)$:

$$\rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_1\sigma_1) = 0 \qquad (3)$$

The probability of finding two electrons with the same spin at the same spatial point vanishes.

In an attempt to quantify the extent of delocalization of the first electron, Bader proceeds as follows.[24] The two-particle distribution function is used to define the function $F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ by

$$F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) \equiv \rho^{(2)}{}_N(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) - \rho_N^{(1)}(\mathbf{r}_1\sigma_1)\,\rho_N^{(1)}(\mathbf{r}_2\sigma_2) \qquad (4)$$

$F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ is a measure of the deviation of the two-particle distribution function from the product $\rho_N^{(1)}(\mathbf{r}_1\sigma_1)\,\rho_N^{(1)}(\mathbf{r}_2\sigma_2)$ of the electron densities at the two points.[25] The sum rules obeyed by $F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ are

$$\int d\mathbf{r}_2 \sum_{\sigma_2} F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) = -\rho_N^{(1)}(\mathbf{r}_1\sigma_1)$$

$$\int d\mathbf{r}_1 \int d\mathbf{r}_2 \sum_{\sigma_2} F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) = -N_{\mathrm{N}}(\sigma_1) \qquad (5)$$

again being independent of the nature of the particles. We also define the quantity

$$F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) \equiv \sum_{\sigma_1,\sigma_2} F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) \qquad (6)$$

which has no dependence on the spin indices. It is this spatial $F_N^{(2)}$ that is used by Bader to characterize the localization and delocalization of an electron.

The integrated quantities, the localization index $\lambda(\mathrm{A})$ and the delocalization index $\delta(\mathrm{A,B})$, are defined by integrating the point–point quantities over the volumes V_A and V_B ascribed to atoms A and B

$$\lambda(\mathrm{A}) \equiv \left|\int_{\mathrm{A}} d\mathbf{r}_1 \int_{\mathrm{A}} d\mathbf{r}_2\, F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\right|$$

$$\delta(\mathrm{A,B}) \equiv 2\left|\int_{\mathrm{A}} d\mathbf{r}_1 \int_{\mathrm{B}} d\mathbf{r}_2\, F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\right| \qquad (7)$$

In contrast to $F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$, the sharing amplitude $\langle\zeta;\zeta'\rangle$ is found solely from single-particle properties and represents the generalization of a simple construct for pure, single-particle states.[21] Let the single-particle wave function be

$$\varphi(\zeta)$$

As is well-known, the wave function multiplied by a constant phase actor does not change the state of the particle. An invariant construct which measures the difference in phase of the wave function at the two points ζ and ζ' is given by

$$\varphi(\zeta)\,\varphi^*(\zeta')$$

The absolute value squared of this quantity is the measure of the sharing (delocalization) of the wave between the two points. The integral of ζ' over all space gives the particle density at the other point:

$$\int d\zeta'\, |\varphi(\zeta)\,\varphi^*(\zeta')|^2 = |\varphi(\zeta)|^2$$

The sharing amplitude $\langle\zeta;\zeta'\rangle$

$$\langle\zeta;\zeta'\rangle = \rho_N{}^{1/2}(\zeta;\zeta') \qquad (8)$$

[dropping the superscript on $\rho_N(\zeta;\zeta')$] is the generalization of $\varphi(\zeta)\varphi^*(\zeta')$ to impure states, and the sharing index

$$I(\zeta;\zeta') \equiv |\langle\zeta;\zeta'\rangle|^2 \qquad (9)$$

is the generalization of $|\varphi(\zeta)\,\varphi^*(\zeta')|^2$. As a result of its construction, the sharing index satisfies the sum rule

$$\int d\zeta'\, I(\zeta;\zeta') = \rho_N(\zeta;\zeta)$$

The amplitude $\langle\zeta;\zeta'\rangle$ can be written in terms of the eigenfunctions and eigenvalues, $\varphi_m(\zeta)$, and eigenvalues, ν_m, of the density matrix (the natural spin−orbitals) as[21]

$$\langle\zeta;\zeta'\rangle = \sum_m \varphi_m(\zeta)\nu_m^{\ 1/2}\varphi_m^*(\zeta')$$

The sharing index, which depends solely upon the spatial coordinates, is formed from the sum of $I(\zeta;\zeta')$ over the spin indices:

$$I(\mathbf{r};\mathbf{r}') \equiv \sum_{\sigma,\sigma'} I(\mathbf{r}\sigma;\mathbf{r}'\sigma')$$

The integrated quantities, I_{AA} and B_{AB}, are

$$I_{AA} \equiv \int_A d\mathbf{r} \int_A d\mathbf{r}'\, I(\mathbf{r};\mathbf{r}')$$

$$B_{AB} \equiv 2I_{AB} \equiv 2\int_A d\mathbf{r} \int_B d\mathbf{r}'\, I(\mathbf{r};\mathbf{r}') \qquad (10)$$

Below there are two systems to which we apply the indices: the first is a particular set of electronic (and bosonic, replacing the electrons by bosons) states of H_2; the second is a classical fluid. It may be objected that because there are only two electrons, H_2 is too special a case to which the definition should be applied. However, H_2 has the prototypical covalent bond and any measure of delocalization should be applicable to the molecule. We could equally well consider Li_2 in which regions containing the core electrons are ignored, the valence regions mimicking the electronic structure of H_2. It may also be objected that a classical fluid does not behave as a collection of fermions. However, at high temperatures and low particle densities a Fermi (and a Bose) gas behaves as a perfect gas.

III. Application to H_2

Here we consider two systems: the first is a Fermi system, where the electrons in H_2 are described by a simple set of singlet wave functions; the second is a Bose system, where the electrons in H_2 are replaced by spin 0 particles also described by a simple set of wave functions. Let $\varphi_s(\mathbf{r})$ and $\varphi_a(\mathbf{r})$ be two single-particle real orbitals, the former being a bonding (σ_g) orbital and the latter an antibonding (σ_u) orbital. For the Fermi system[26] the wave functions are

$$\Psi_{FD,\theta}(\zeta_1,\zeta_2) \equiv [\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\cos\theta - \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\sin\theta] \times [\alpha(\sigma_1)\,\beta(\sigma_2) - \beta(\sigma_1)\,\alpha(\sigma_2)]/\sqrt{2} \qquad (11)$$

the spin functions being denoted by $\alpha(\sigma)$ and $\beta(\sigma)$, and the singly excited wave function

$$\Psi_{FD}(\zeta_1,\zeta_2) \equiv \frac{1}{2}[\varphi_s(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2) + \varphi_a(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)][\alpha(\sigma_1)\,\beta(\sigma_2) - \beta(\sigma_1)\,\alpha(\sigma_2)] \qquad (12)$$

Values of the mixing angle θ giving unique wave functions up to an overall phase factor may be restricted to lie in the interval $-\pi/2 < \theta \le \pi/2$. For the Bose system the wave functions are

$$\Psi_{BE,\theta}(\mathbf{r}_1,\mathbf{r}_2) \equiv [\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\cos\theta - \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\sin\theta] \qquad (13)$$

and

$$\Psi_{BE}(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{1}{\sqrt{2}}[\varphi_s(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2) + \varphi_a(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)] \qquad (14)$$

(These latter are just the spatial parts of the Fermi wave functions.)

Although simple, these sets of wave functions have the flexibility of being able to mimic the behaviors of a variety of states of fermionic and bosonic H_2, ranging from single determinant ground and doubly excited state wave functions to wave functions which include the effects of correlation of the electrons as well as including a wave function which describes singly excited states.

For both the Fermi and Bose wave functions having the parametric dependence on θ the spinless point−point quantities are

$$\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = 2\{\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\cos\theta - \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\sin\theta\}^2$$

$$F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -2\{\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\cos\theta + \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\sin\theta\}^2 + 4[\varphi_s(\mathbf{r}_1)^2 - \varphi_a(\mathbf{r}_1)^2][\varphi_s(\mathbf{r}_2)^2 - \varphi_a(\mathbf{r}_2)^2]\cos^2\theta\sin^2\theta$$

$$I(\mathbf{r};\mathbf{r}') = 2\{\varphi_s(\mathbf{r})\,\varphi_s(\mathbf{r}')|\cos\theta| + \varphi_a(\mathbf{r})\,\varphi_a(\mathbf{r}')|\sin\theta|\}^2 \qquad (15)$$

The spinless point−point quantities for the singly excited wave functions are, for both the Fermi and Bose functions,

$$\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = \{\varphi_s(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2) + \varphi_a(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\}^2$$

$$F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -\{\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2) - \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\}^2$$

$$I(\mathbf{r};\mathbf{r}') = \{\varphi_s(\mathbf{r})\,\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})\,\varphi_a(\mathbf{r}')\}^2 \qquad (16)$$

That both the Fermi and Bose wave functions lead to precisely the same expressions for the spatial two-particle distribution function and to the point−point Bader index is a strong indication that the Fermi hole in general has nothing to do with the delocalization of a particle.

There are some characteristic features of these expressions which should be noted. Consider the expressions given in eqs 15. First, as is well-known, when the wave function is given by a single determinant and $\mathbf{r}_1$ is identified with $\mathbf{r}$ and $\mathbf{r}_2$ with $\mathbf{r}'$, the point−point Bader index $F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and the point−point sharing index $I(\mathbf{r};\mathbf{r}')$ are identical. This occurs for $\theta = 0$ and for $\theta = \pi/2$. Second, when $\cos\theta\sin\theta$ is less than 0 the two-particle distribution function $\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and the sharing index $I(\mathbf{r};\mathbf{r}')$, again with the identifications of $\mathbf{r}_1 = \mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r}'$, are equal. Third, when $\cos\theta\sin\theta$ is greater than 0 the difference between the Bader index $F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and the sharing index $I(\mathbf{r};\mathbf{r}')$ resides solely in the term

$$4[\varphi_s(\mathbf{r}_1)^2 - \varphi_a(\mathbf{r}_1)^2][\varphi_s(\mathbf{r}_2)^2 - \varphi_a(\mathbf{r}_2)^2]\cos^2\theta\sin^2\theta$$

the difference between the indices being a maximum when $\theta = \pi/4$. When the volume−volume indices are found by integrating over the atomic basins, the difference due to this term vanishes. This vanishing may in part account for the rough agreement between the basin−basin sharing indices and the values of the delocalization indices which was found by Wang and Werstiuk.[8] Lastly, we note that the expressions given in eqs 16 for the singly excited states all differ. In particular note the difference in the relative signs of the products of orbitals $\varphi_s\varphi_s$ and $\varphi_a\varphi_a$ in the expressions for $F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and $I(\mathbf{r};\mathbf{r}')$.

The sharing amplitudes are given by

$$\langle \zeta;\zeta' \rangle_{\mathrm{FD},\theta} = \delta_{\sigma,\sigma'}\{\varphi_s(\mathbf{r})|\cos(\theta)|\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})|\sin(\theta)|\varphi_a(\mathbf{r}')\}$$

$$\langle \zeta;\zeta' \rangle_{\mathrm{FD}} = \frac{1}{\sqrt{2}}\delta_{\sigma,\sigma'}\{\varphi_s(\mathbf{r})\,\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})\,\varphi_a(\mathbf{r}')\} \quad (17)$$

for the Fermi system and

$$\langle \mathbf{r};\mathbf{r}' \rangle_{\mathrm{BE},\theta} = \sqrt{2}\{\varphi_s(\mathbf{r})|\cos(\theta)|\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})|\sin(\theta)|\varphi_a(\mathbf{r}')\}$$

$$\langle \mathbf{r};\mathbf{r}' \rangle_{\mathrm{BE}} = \{\varphi_s(\mathbf{r})\,\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})\,\varphi_a(\mathbf{r}')\} \quad (18)$$

for the Bose system, the amplitudes for the Bose system being essentially the spatial part of the amplitudes for the Fermi system. The quantities obtainable from the two-particle distribution function have no counterparts to these single-particle amplitudes.

The spin independent course grained quantities, i.e., the various volume−volume indices including the two-particle distribution function, are found by integrating the point−point quantities over the volumes constituting the atoms according to Bader's criterion.[27] Label the atoms by A and B. The volumes associated with the atoms are simple: the atomic volumes are separated by a plane which is perpendicular to and bisects the line connecting the two nuclei. For the wave functions depending on θ the indices are, for both the Fermi and the Bose systems (the integrated values of the point−point distribution function are denoted by P_{AA} and P_{AB})[28]

$$\lambda(A) = \frac{1}{2}[1 + 8|(\varphi_s,\varphi_a)_A|^2 \cos\theta \sin\theta]$$

$$\delta(\mathrm{A,B}) = 1 - 8|(\varphi_s,\varphi_a)_A|^2 \cos\theta \sin\theta$$

$$I_{AA} = \frac{1}{2}[1 + 8|(\varphi_s,\varphi_a)_A|^2|\cos\theta \sin\theta|]$$

$$B_{AB} = 1 - 8|(\varphi_s,\varphi_a)_A|^2|\cos\theta \sin\theta|$$

$$P_{AA} = \frac{1}{2} - 4|(\varphi_s,\varphi_a)_A|^2 \cos\theta \sin\theta$$

$$P_{AB} = \frac{1}{2} + 4|(\varphi_s,\varphi_a)_A|^2 \cos\theta \sin\theta \quad (19)$$

For the singly excited wave functions we obtain, again for both the Fermi and Bose systems,

$$\lambda(\mathrm{A}) = \frac{1}{2} - 2|(\varphi_s,\varphi_a)_A|^2$$

$$\delta(\mathrm{A,B}) = 1 + 4|(\varphi_s,\varphi_a)_A|^2$$

$$I_{AA} = \frac{1}{2} + 2|(\varphi_s,\varphi_a)_A|^2$$

$$B_{AB} = 1 - 4|(\varphi_s,\varphi_a)_A|^2$$

$$P_{AA} = \frac{1}{2} + 2|(\varphi_s,\varphi_a)_A|^2$$

$$P_{AB} = \frac{1}{2} - 2|(\varphi_s,\varphi_a)_A|^2 \quad (20)$$

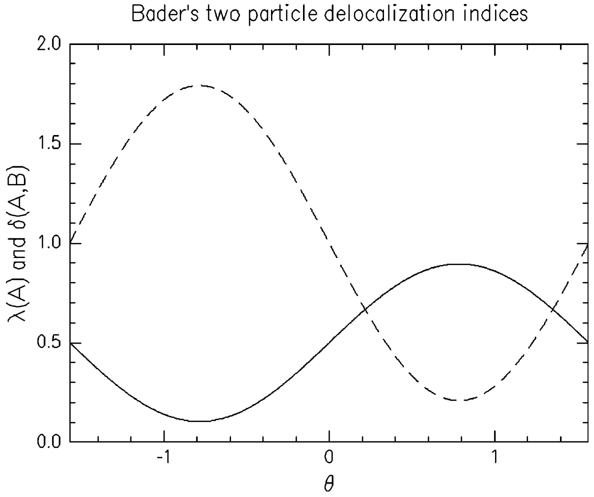

Figure 1. Integrated Bader two-particle delocalization indices as functions of the mixing angle θ in radians.

To illustrate quantitatively the differences between the two-particle distribution function, the Bader indices, and the sharing indices, we choose particularly simple orbitals: let $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ be hydrogen-like 1s orbitals of the form

$$\phi_{A,B}(\mathbf{r}) = (\alpha^3/\pi)^{1/2} e^{-\alpha|\mathbf{r}-\mathbf{r}_{A,B}|}$$

centered on the protons A and B, respectively. The exponent α is chosen to be 1.18, a compromise[21] among a molecular orbital type wave function, the Heitler−London−Wang wave function and the Weinbaum wave function. The distance between the nuclei is chosen to be $R = 1.403$ u. The forms of the molecular orbitals are

$$\varphi_s(\mathbf{r}) = \frac{1}{\sqrt{2(1+S)}}[\phi_A(\mathbf{r}) + \phi_B(\mathbf{r})]$$

$$\varphi_a(\mathbf{r}) = \frac{1}{\sqrt{2(1-S)}}[\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})]$$

The choices of the exponent and the internuclear distance give

$$S = 0.682$$

and

$$(\varphi_s,\varphi_a)_A = 0.4448$$

The Weinbaum wave function[29] is characterized by $\theta = 0.111$, and the valence bond wave function is characterized by $\theta = 0.187$.

We first compare the integrated quantities, the Bader indices and the corresponding basin-basin sharing indices, and then consider the basin−basin two-particle distribution functions. In Figures 1−3 the solid lines represent the self-basin indices λ(A), I_{AA}, and the self-two-particle distribution index, P_{AA}, and the dashed lines represent the inter-basin indices δ(A,B), B_{AB}, and the inter-basin distribution index, P_{AB}. As noted above, the Bader indices and the sharing indices coincide for values of θ ranging from 0 to $\pi/2$: $\lambda(\mathrm{A}) = I_{AA}$ and $\delta(\mathrm{A,B}) = B_{AB}$. However, for values of θ between $-\pi/2$ and 0, the indices behave quite differently: the localization index λ(A) of Bader drops below 0.5 by as much as the self-sharing index I_{AA} rises above 0.5 and the delocalization index δ(A,B) rises above 1.0 by as much as the bond index B_{AB} drops below 1.0. That the integrated

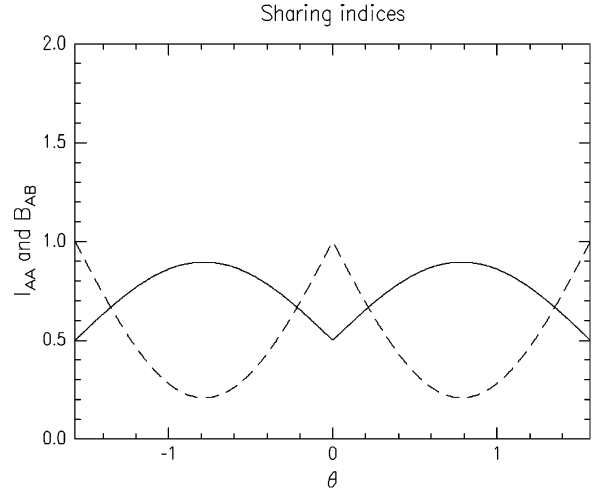

Figure 2. Integrated sharing indices as functions of the mixing angle θ in radians.

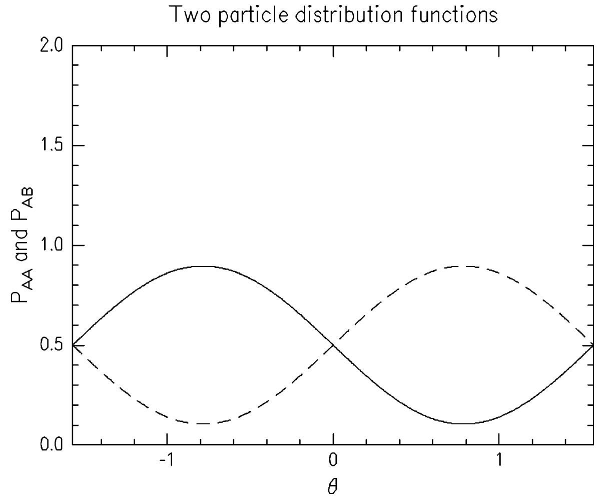

Figure 3. Integrated two-particle distribution functions as functions of the mixing angle θ in radians.

sharing indices do not discriminate between positive and negative values of the mixing angle θ should not be a surprise because the single-particle density matrix

$$\rho(\zeta;\zeta') = \delta_{\sigma,\sigma'}\{\varphi_s(\mathbf{r})\cos^2(\theta)\,\varphi_s(\mathbf{r}') + \varphi_a(\mathbf{r})\sin^2(\theta)\,\varphi_a(\mathbf{r}')\}$$

does not disciminate between the positive and negative values. Therefore no single-particle property can discriminate between these values.

The two-particle distribution indices P_{AA} and P_{AB}, given in Figure 3, indicate that the correlation introduced into the wave function for positive values of θ tends to keep the two electrons apart, the inter-basin index P_{AB} increasing above 0.5 and the self-index P_{AA} decreasing below 0.5. When θ is negative, the correlation is reversed: the two electrons are more likely to be in the same basin than in different basins.

Can the contrasting behaviors of the Bader indices and the sharing indices be understood from the wave function directly? Rather than considering the Bader indices, it is simpler at the outset to understand the behavior of the two-particle distribution function. Consider the spatial part only of the Fermi function

$$\Psi_\theta(\mathbf{r}_1,\mathbf{r}_2) \equiv [\varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)\cos\theta - \varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)\sin\theta]$$

When $\theta = 0$ or $\theta = \pi/2$, the functions are simple, being the products of either the bonding or the antibonding molecular orbitals

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2) = \varphi_s(\mathbf{r}_1)\,\varphi_s(\mathbf{r}_2)$$

$$\Psi_{\pi/2}(\mathbf{r}_1,\mathbf{r}_2) = -\varphi_a(\mathbf{r}_1)\,\varphi_a(\mathbf{r}_2)$$

As a result, there is no correlation between the positions of the two electrons. Particle 2 is independent of particle 1. If we fix particle 2 at some position, e.g., $\mathbf{r}_2$, where the single-particle orbital does not vanish, the behavior of the other particle is described by the orbital $\varphi_s(\mathbf{r}_1)$ when the total wave function is $\Psi_0(\mathbf{r}_1,\mathbf{r}_2)$ and by the orbital $\varphi_a(\mathbf{r}_1)$ when the total wave function is $\Psi_{\pi/2}(\mathbf{r}_1,\mathbf{r}_2)$, irrespective of the value of $\mathbf{r}_2$. Because each of the orbitals extends over the entire molecule, particle 1 is delocalized over the entire molecule.

For wave functions which are not single determinants it is simplest to consider the case in which the atomic orbitals $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ have no overlap, $S = 0$. The various integrated quantities behave similarly to those given in Figures 1−3, the difference being that the extreme values of the indices for λ(A) are 0 and 1; for δ(A,B), 0 and 2; for I_{AA}, 0.5 and 1; and for I_{AB}, 0 and 1. The locations of these extremes occur at the same values of θ as when the overlap is nonzero. Consider first the case of $\theta = \pi/4$. The spatial part of the Fermi wave function is simply the valence bond wave function when there is zero overlap

$$\Psi_{\pi/4}(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{1}{\sqrt{2}}[\phi_A(\mathbf{r}_1)\,\phi_B(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\,\phi_A(\mathbf{r}_2)]$$

We begin with a discussion of the two-particle distribution function. When particle 1 is in the vicinity of nucleus A, particle 2 must be in the vicinity of nucleus B for the wave function to be nonvanishing and vice versa. This is the behavior indicated by the values of the integrated two-particle distribution function, $P_{AA} = 0$ and $P_{AB} = 1$, in the case of zero overlap, and reflected by the values given in the Figure 3 for $\theta = \pi/4$ when the overlap is nonvanishing. The values of the sharing indices can also be understood on the basis of the wave function. To get the behavior of a single particle, e.g., particle 1, we first choose particle 2 to be in the vicinity of nucleus B. Then that part of the wave function referring to particle 1 which is nonvanishing is $\phi_A(\mathbf{r}_1)$, and particle 1 is localized in the vicinity of nucleus A. If particle 2 is in the vicinity of nucleus A, the situation is reversed and that part of the wave function referring to particle 1 is $\phi_B(\mathbf{r}_1)$, localizing particle 1 in the vicinity of basin B. In either case, particle 1 is localized in the vicinity of a single basin resulting in the value of 1 for the self-sharing index I_{AA} when $S = 0$ and $\theta = \pi/4$. Correspondingly the interbasin index is a minimum, $B_{AB} = 0$. These extreme values are reflected in Figure 2 when the overlap is nonvanishing. What do the Bader indices give? These follow immediately from the definitions in terms of the two-particle distribution function and the one-particle density, $\lambda(A) = 1$, and $\delta(A,B) = 0$. The values of the integrated Bader indices agree with those given by the integrated sharing indices.

The behavior of the Bader indices and the sharing indices show completely disparate behaviors for negative values of θ. Consider the case of $\theta = -\pi/4$ when there is zero overlap of the atomic functions. The spatial part of the wave function is

$$\Psi_{-\pi/4}(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{1}{\sqrt{2}}[\phi_A(\mathbf{r}_1)\,\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_1)\,\phi_B(\mathbf{r}_2)]$$

TABLE 1: Values of Various Indices for the Singly Excited Wavefunction

index	value
P_{AA}	0.896
P_{AB}	0.104
λ(A)	0.104
δ(A,B)	1.791
I_{AA}	0.896
B_{AB}	0.209

The behavior of the two-particle distribution function can be simply read off; if particle 2 is in the vicinity of nucleus A, then so is particle 1. The integrated two-particle distribution functions reflect this: the values of the indices are $P_{AA} = 1$ and $P_{AB} = 0$. The behavior of the single-particle sharing indices is also readily apparent. Fix particle 2 to be in the vicinity of nucleus A. Then particle 1 is described by the orbital $\phi_A(\mathbf{r}_1)$, which is also localized in the vicinity of nucleus A. If, rather, particle 2 is fixed in the vicinity of nucleus B, then particle 1 is described by $\phi_B(\mathbf{r}_1)$, which is localized in the vicinity of nucleus B. In either case, particle 1 is localized in the region of a single basin, giving rise to the values of the single-particle sharing quantities, $I_{AA} = I_{BB} = 1$ and $B_{AB} = 0$. Aside from the overall sign, the Bader indices require the subtraction of 1 from the two-particle distribution functions, followed by multiplication by 2 for the interbasin index. This gives the values of $\lambda(A) = |F(A,A)| = 0$ and $\delta(A,B) = 2|F(A,B)| = 2$ when there is zero overlap of the atomic orbitals. According to the interpretation of the Bader indices,[3,5] $|F(A,A)| = 0$ indicates that no particles are localized in basin A and $|F(A,B)| = 1$ indicates that a single particle, referenced to atom A, is delocalized onto atom B, and a single particle, referenced to atom B, is delocalized onto atom A. This, however, is not what is given by the two-particle distribution function or indicated by the wave function, both of which quite clearly indicate that the two-particles behave as a “bound” pair. At the two electron level, the particles, as a pair, are shared between basins A and B. The interpretation which has been given to the Bader indices does not reflect this.

The values of the integrated indices for the singly excited wave functions when $S = 0.682$ are given in Table 1. These values are, in fact, the same as those obtained from the wave function $\Psi_{-\pi/4}(\mathbf{r}_1,\mathbf{r}_2)$. It should be noted that the value of δ(A,B) in the table does not agree with the result given by Fradera and Solà in ref 6.[30] The integrated two-particle distribution functions reflect the localized pairing of the two-particles in either one or the other of the two basins. If one particle is in basin A, for example, there is a high probability that the other particle is also in basin A and there is a small probability that the other particle is in basin B. The sharing indices reflect a similar behavior. A single particle is localized in either one basin or the other, with a small amount of interbasin sharing. Again, the integrated Bader indices do not reflect this. Instead, the interpretation suggested for the Bader indices is almost complete delocalization of the electrons between the basins.

A naive determination of the bond order for this wave function that contains one bonding and one antibonding orbital is 0, a value much closer to the value of the interbasin sharing index B_{AB} than to the value of the Bader index δ(A,B), although perhaps not pertinent to the establishment of the validity of the indices. But the point−point single-particle sharing amplitude, given in Figure 17 below, indicates, in addition, that this is an antibonding type of sharing rather than a bonding type of sharing, again more in line with what should be expected for the singly excited state. The two-particle distribution function has no counterpart to the sharing amplitude and does not distinguish between bonding and antibonding types of delocalization.

As in the former case, it is simplest to dissect the behavior of the wave function in the special case of zero overlap. The spatial part of the wave function is then

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) \equiv \frac{1}{\sqrt{2}}[\phi_A(\mathbf{r}_1)\,\phi_A(\mathbf{r}_2) - \phi_B(\mathbf{r}_1)\,\phi_B(\mathbf{r}_2)]$$

when written in terms of the atomic orbitals. What differs from the wave function $\Psi_{-\pi/4}$ is the relative sign between the two terms; the present wave function has a node between the simple pair wave functions, $\phi_A(\mathbf{r}_1)\,\phi_A(\mathbf{r}_2)$ centered on nucleus A and $\phi_B(\mathbf{r}_1)\,\phi_B(\mathbf{r}_2)$ centered on nucleus B. Because the atomic orbitals have zero overlap, the analysis of the behavior of the particles is precisely the same as that given for the previous wave function, with the values of the various integrated indices being the same. Again, the Bader indices do not reflect the localization of the pair of electrons.

Recall that the Bader indices involve the difference between the product of the number of particles in the basins and the integrated two-particle distribution function. This can obscure the meaning of the Bader indices. In this case, it is because the number of particles in each basin is 1 and the integrated interbasin distribution function is small that the difference is sizable, leading to the large value of δ(A,B). The origin is in the behavior of the two-particle distribution function itself and I think that the simplest interpretation is a direct interpretation of the two-particle distribution function; namely, the particles are mainly paired in either one or the other basin.

Next we compare some of the point−point Bader indices and point−point sharing indices for both positive θ and negative θ. Although for positive θ the integrated Bader indices and sharing indices have the same values, the point−point Bader indices and the point−point sharing indices differ. When θ is negative, it is clear from the integrated indices that the point−point indices must differ. The spatial parts of the point−point indices (and amplitudes) depend on six variables. We reduce the number of quantities being varied in the figures by fixing the internuclear axis to be along the x axis, by fixing the midpoint of the molecule at the origin of the coordinate system, and by placing one point ($\mathbf{r}'$, the fixed point) on the proton located at negative x. The other point is allowed to roam about the xy plane. The vertical axis is the value of the quantity being plotted. It should be noted that the figures give but a small subset of the point−point quantities and quantitative values of the integrated indices cannot be inferred from the figures. Recall that for the chosen set of wave functions, the values of the indices which depend only on the spatial coordinates are identical for the Fermi particles and Bose particles.

The Bader indices and the sharing indices have the same values for single determinant wave functions when the identifications $\mathbf{r} = \mathbf{r}_1$ and $\mathbf{r}' = \mathbf{r}_2$ are made. Figures 4 and 5 give the point−point indices for the two single determinant wave functions in the set of wave functions, Figure 4 for $\theta = 0$ and Figure 5 for $\theta = \pi/2$. The first is representative of a Hartree−Fock ground state, and the second represents a “Hartree−Fock” doubly excited state when describing electrons. Both sets of indices are symmetric with respect to inversion through the origin, and indeed reflect the behavior of the squares of the molecular orbitals $\varphi_s(\mathbf{r})$ and $\varphi_a(\mathbf{r})$, respectively. A major difference between the two figures is that the point−point

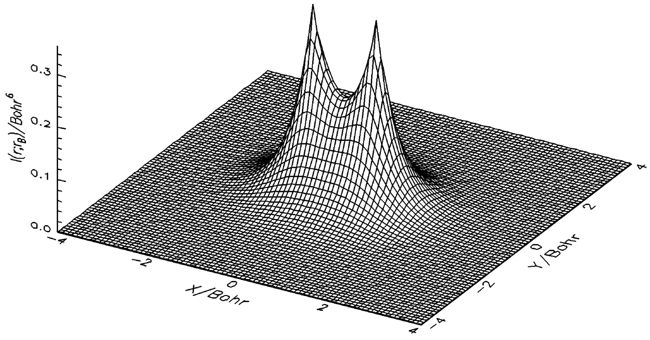

Figure 4. Point–point sharing and Bader indices, $\theta = 0°$.

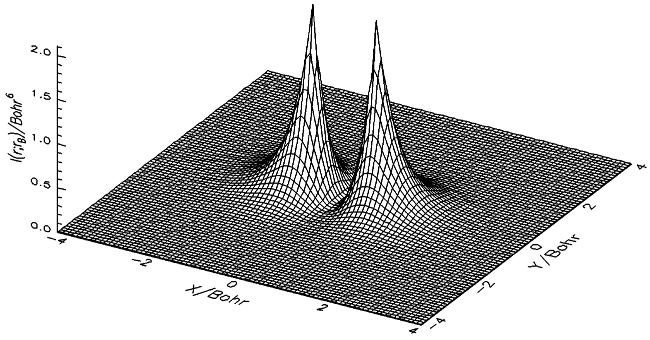

Figure 5. Point–point sharing and Bader indices, $\theta = 90°$.

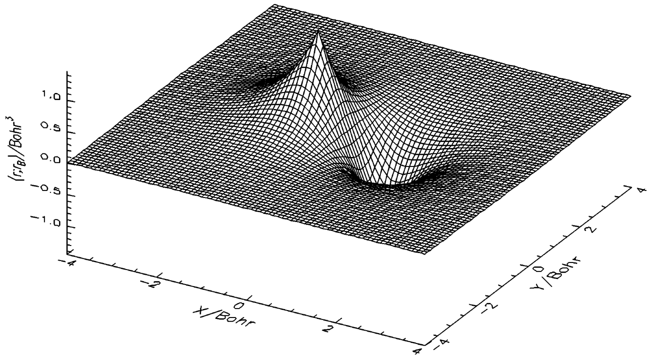

Figure 6. Sharing amplitude, $\theta = 90°$.

indices in Figure 5 dip to naught on the line having $x = 0$ in contrast to the nonzero value in Figure 4. This is a reflection of a possible nodal surface of the molecular orbital $\varphi_a(\mathbf{r})$ cutting the *xy* plane. But this node can only be inferred from the quantities derived from the two-particle distribution function. The sharing amplitude for the wave function having $\theta = \pi/2$, given in Figure 6, shows the node unambiguously, there being a change in the sign of the amplitude as the node is crossed. In the present case the amplitude clearly has the hallmarks of antibonding rather than bonding. This is one illustration of an aspect of the sharing quantities that is not conveyed by the two-particle indices: in general, the sharing amplitudes have nodal surfaces. It might be noted that the node is not at all picked up by the integrated quantities, the values of the interbasin indices being 1 for both the ground Hartree–Fock state and the excited Hartree–Fock state. These results indicate that the point–point indices have the advantage over the integrated quantities of discriminating between the behaviors of the electrons in the ground electronic state and in the doubly excited state. The sharing amplitude, however, provides the greatest discrimination between the behavior of the electrons in the two states.

As noted above, the Weinbaum wave function, a simple wave function including effects due to correlation, is specified by the value $\theta = 0.111$. The point–point sharing index and the point–point Bader index are given in Figures 7 and 8 for this wave function.[31] Superficially, the indices are similar. Unlike the indices represented in Figure 4 in which the peaks at the two protons are of equal height, in this case the peaks located at the fixed point are higher than the peaks at the other proton. As indicated in Figure 7, correlation has the effect of localizing an electron to the vicinity of the fixed point on the proton. A similar effect occurs for the Bader index in Figure 8; however here, as shown by the plot of the two-particle distribution function in Figure 9, the effect is due to two factors: (1) the increase in the probability of finding the second particle about the second proton if the first is in the vicinity of the first proton and (2) the definition of $F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ as the difference between the two-particle distribution function and the product of the single-particle densities at the two points.

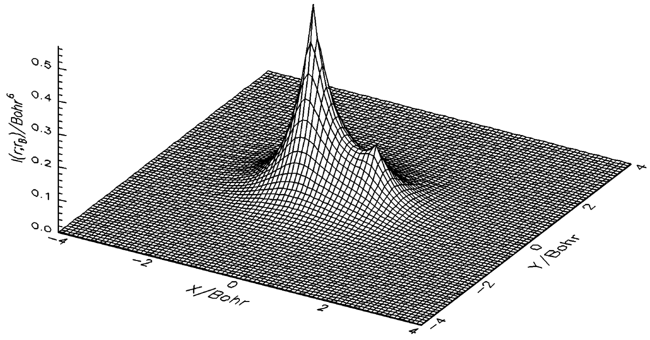

Figure 7. Point–point sharing index, $\theta = 6.36°$.

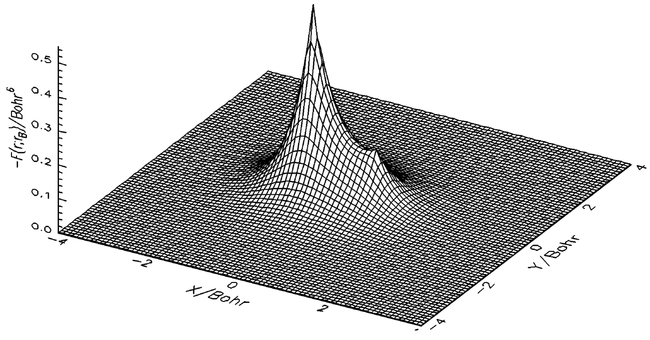

Figure 8. Bader point–point delocalization index, $\theta = 6.36°$.

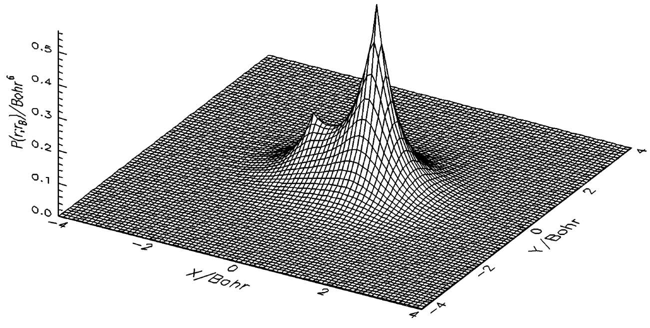

Figure 9. Two-particle distribution function, $\theta = 6.36°$.

Closer inspection of Figures 7 and 8 indicates that the peak at the fixed point (the proton located at negative *x*) is higher for the sharing index than for the Bader index. The peak at the second proton is also higher and sharper for the sharing index than for the Bader index. This difference is indicated more clearly by Figure 10 in which the difference between the indices, $[-F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)] - I(\mathbf{r};\mathbf{r}')$ with the identifications $\mathbf{r}_1 = \mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r}'$, is plotted. In contrast to the two sets of integrated quantities that have the same values when θ is positive, the point–point indices differ.

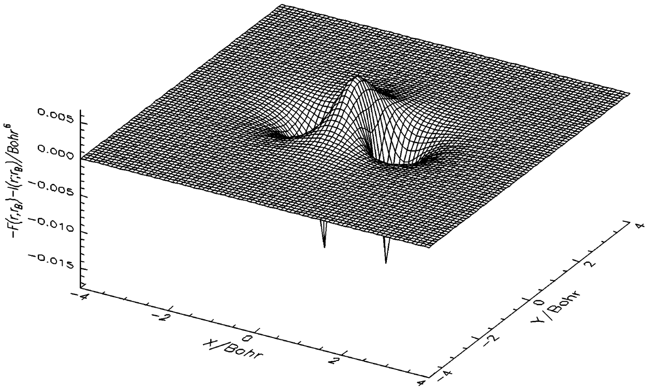

Figure 10. Difference between the point−point Bader index and sharing index, $\theta = 6.36°$.

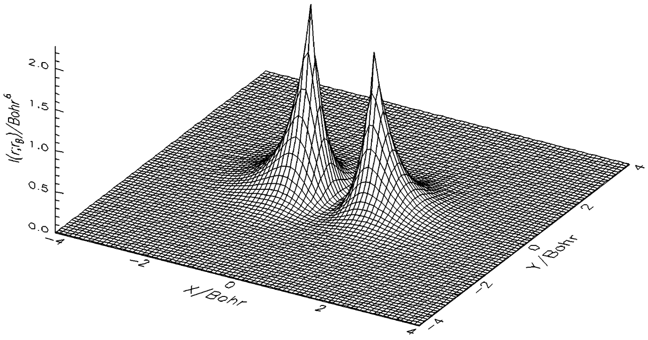

Figure 11. Point−point sharing index, $\theta = -83.64°$.

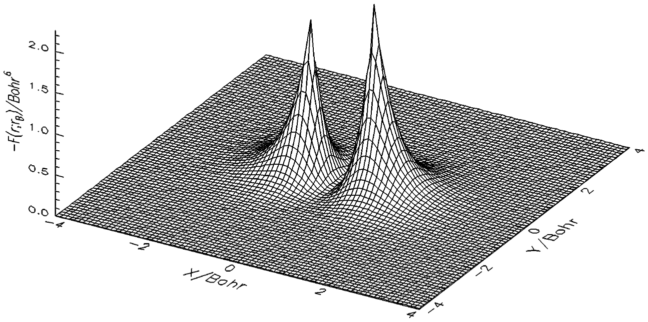

Figure 12. Point−point Bader delocalization index, $\theta = -83.64°$.

The point−point indices for the wave function that is orthogonal to the Weinbaum function are given in Figure 11 for the sharing index and in Figure 12 for the Bader index. We note that the sharing index is more localized in the region surrounding the fixed point and the Bader index is more localized about the other proton, both consistent with the differing values of the integrated sharing indices and Bader indices, $I_{AA} = 0.587$ and $B_{AB} = 0.826$ in contrast to $\lambda(A) = 0.413$ and $\delta(A,B) = 1.174$. In addition, the small value (perhaps zero) of the indices on a line running roughly parallel to the y axis suggests that the sharing is of an antibonding type. When the sharing amplitude is plotted (not shown), this is indeed the case. This behavior fits nicely with the wave function being an excited state.

As a further example of the difference between the point−point quantities when the integrated indices are the same, we give the sharing index and the Bader index in Figures 13 and 14 when the angle θ is 20°. The point−point sharing index is always positive with essentially no sharing from the fixed point to the vicinity of the other proton while the Bader index, although concentrated mainly about the fixed point with a maximum which is lower than that of the sharing index, is negative in the region of the other proton. The two indices show quite different behaviors for this mixing angle.

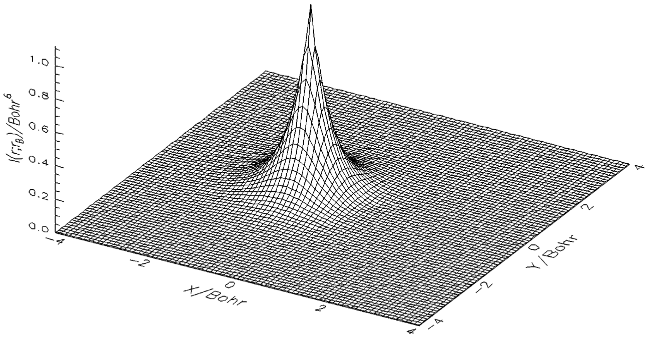

Figure 13. Point−point sharing index, $\theta = 20°$.

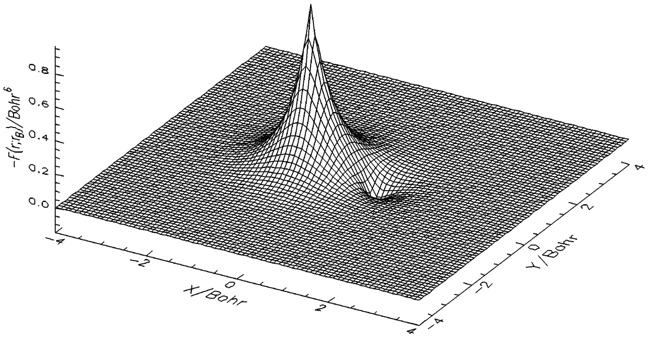

Figure 14. Point−point Bader delocalization index, $\theta = 20°$.

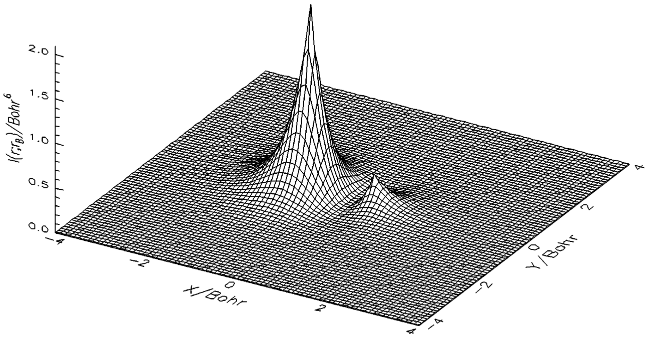

Figure 15. Point−point sharing index, singly excited state.

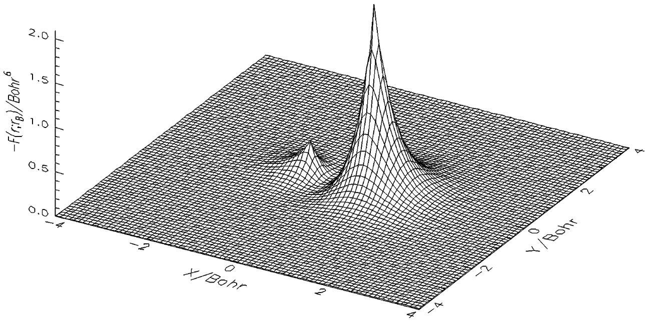

Figure 16. Point−point Bader delocalization index, singly excited state.

The last comparison of the point−point indices is for the singly excited wave functions. The integrated indices, given above in Table 1, show dramatic differences between the sharing quantities and the Bader quantities. The sharing index, given in Figure 15, and the Bader index, given in Figure 16, are also quite different. The point−point sharing index indicates that the electron is localized in the region of the fixed point with rather minor sharing to the vicinity of the second proton whereas the main contribution to the point−point Bader index is from the region surrounding the second proton and a minor contribu-

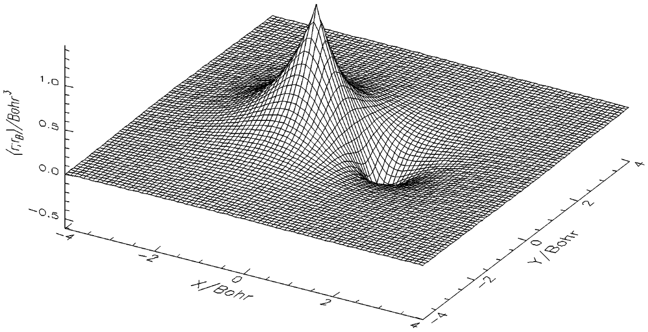

Figure 17. Sharing amplitude, singly excited state.

tion from the region of the fixed point. These differences in the point−point indices are consistent with the differences in the integrated indices, the integrated sharing index indicating localization in one basin is larger than the delocalization to the other basin, the Bader indices indicating just the opposite.

The sharing amplitude for the singly excited wave function is given in Figure 17. As noted above in connection with the integrated indices for this wave function, the sharing amplitude indicates that the sharing is of an antibonding nature. The amplitude is positive in the region around the fixed point with a nodal surface separating that region and the negative region surrounding the other proton. Unlike the amplitude for the doubly excited state at the single determinant level given in Figure 6, the amplitude for the present wave function is not antisymmetric with respect to reflection through the plane containing the midpoint of and perpendicular to the line connecting the two protons. The magnitude of the amplitude is larger at the fixed point than at the location of the other proton. This is a manifestation of the correlation inherent in the singly excited wavfunction.

The results presented in this section indicate that the Bader indices and the sharing indices measure quite different aspects of the behavior of particles in quantal systems. Even when the integrated indices have the same values, the point−point indices generally differ. The exceptions to this are when the wave functions (for electrons) are given by single determinants. One important quantity given by the sharing quantities and not by quantities based on the two-particle distribution function is the sharing amplitude, which allows for the discrimination between bonding and antibonding behavior.

IV. Classical Fluids

In addition to the differences shown above, the indices also differ in the classical limit. Consider a mixture of classical ideal gases in thermal equilibrium at temperature T. The gas is confined to a volume V. The components of the gas are labeled by the index σ. (σ may, but need not, be a spin index.) The total number of σ particles is denoted by N_σ. The two-particle distribution function is

$$\rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) = \frac{N_{\sigma_1}N_{\sigma_2} - \delta_{\sigma_1\sigma_2}N_{\sigma_2}}{V^2} \tag{21}$$

$F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ is given by

$$F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2) = -\delta_{\sigma_1\sigma_2}\frac{N_{\sigma_2}}{V^2} \tag{22}$$

Let the volume associated with A be V_A and that associated with B be V_B. (V_A and V_B need not sum to the total volume.) The Bader indices are given by

$$\lambda(\mathrm{A}) = N_\mathrm{A}\frac{V_\mathrm{A}}{V} = \frac{{N_\mathrm{A}}^2}{N}$$
$$\delta(\mathrm{A,B}) = 2N_\mathrm{A}\frac{V_\mathrm{B}}{V} = 2\frac{N_\mathrm{A}N_\mathrm{B}}{N} \tag{23}$$

where $N_\mathrm{A,B}$ are the total numbers of particles in the volumes $V_\mathrm{A,B}$ and N is the total number of particles in the system. According to the proposed interpretation of $\lambda(\mathrm{A})$, only the fraction N_A/N of the N_A particles in volume V_A are localized in that volume. In turn, the value of $\delta(\mathrm{A,B})$ indicates that there is a long-range delocalization of particles between even well-separated volume V_A and V_B. But to what extent is the reference particle in an ideal gas spread out by quantum effects? It is expected to be of the order of the thermal de Broglie wavelength[32]

$$\Lambda = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$

where m is the mass of the particle, k is Boltzmann's constant, and h is Planck's constant. At high temperature (e.g., in the classical limit) this wavelength is vanishing small, so that quantally the reference particle is not spread out but is in fact localized. The measures proposed by Bader,[3] however, indicate "Fermi correlation" within the volume V_A and delocalization between the two volumes V_A and V_B, which is interpreted as being due to a Fermi hole. But these cannot be due to a Fermi hole in this classical gas because there is no Fermi hole in this classical system! Furthermore, at high temperatures Fermi and Bose gases have identical behaviors, both giving the same localization and delocalization indices, yet a Bose gas has no Fermi hole.

These considerations can also be simply extended to any uniform classical fluid. For simplicity, consider a uniform one-component ($\sigma = 1$) fluid confined to the volume V. The regions associated with A and B are chosen far apart. In a closed system of N particles contained in a volume V, the asymptotic value of the two-particle distribution function is[33]

$$\rho_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)|_{|\mathbf{r}_2-\mathbf{r}_1|\mathrm{large}} \rightarrow \frac{N^2}{V^2}\left(1 - \frac{kT\kappa_T}{V}\right) \tag{24}$$

where κ_T is the coefficient of isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \tag{25}$$

As a consequence, the asymptotic limit of $F_N^{(2)}$ is

$$F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)|_{|\mathbf{r}_2-\mathbf{r}_1|\mathrm{large}} \rightarrow -\frac{N^2}{V^2}\frac{kT\kappa_T}{V} \tag{26}$$

and the index $\delta(\mathrm{A,B})$ between the two widely separated volumes containing N_A and N_B particles respectively is

$$\delta(\mathrm{A,B}) = 2N_\mathrm{A}N_\mathrm{B}\frac{kT\kappa_T}{V} \tag{27}$$

a result that agrees with the calculation for an ideal gas and that does not vanish unless the fluid is incompressible. Again, this asymptotic result is for a purely classical system for which there is no Fermi hole.

The sharing amplitude and the associated sharing index stand in sharp contrast to the Bader indices. These are readily calculated for a single particle in an ideal gas. In the following we ignore any contribution due to the spin of the particles. The normalized distribution function which plays the role of an occupation number is

$$\rho(\mathbf{p}) = \frac{e^{-\mathbf{p}^2/2mkT}}{q}$$

q is the partition function

$$q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

V is the volume of the gas, and $\mathbf{p}$ is the momentum. The normalized natural orbitals are the eigenfunctions of momentum operator

$$\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{h^{3/2}} e^{i\mathbf{r}\cdot\mathbf{p}/\hbar}$$

To get the sharing amplitude, we form the square root of $\rho(\mathbf{p})$, multiply by $\psi_{\mathbf{p}}(\mathbf{r})\,\psi^*_{\mathbf{p}}(\mathbf{r}')$ and by the square root of the number of particles N in the gas, and then integrate over the momentum. This gives

$$\begin{aligned}\langle \mathbf{r};\mathbf{r}'\rangle &= \left(\frac{N}{q}\right)^{1/2} \int d\mathbf{p}\; \psi_{\mathbf{p}}(\mathbf{r}) e^{-\mathbf{p}^2/4mkT} \psi^*_{\mathbf{p}}(\mathbf{r}') \\ &= \bar{\rho}^{1/2} \left(\frac{8\pi mkT}{h^2}\right)^{3/4} e^{-mkT(\mathbf{r}-\mathbf{r}')^2/\hbar^2}\end{aligned}$$

$\bar{\rho}$ is the density of the gas N/V. The corresponding point–point sharing index is

$$I(\mathbf{r};\mathbf{r}') = |\langle \mathbf{r};\mathbf{r}'\rangle|^2 = \bar{\rho}\left(\frac{8\pi mkT}{h^2}\right)^{3/2} e^{-2mkT(\mathbf{r}-\mathbf{r}')^2/\hbar^2}$$

As the thermal de Broglie wavelength Λ becomes small, the sharing amplitude and the sharing index become more localized to the region for which $(\mathbf{r} - \mathbf{r}')^2 < \hbar^2/2mkT$. In the limit of zero de Broglie wavelength we find[34]

$$\lim_{\Lambda\to 0} I(\mathbf{r};\mathbf{r}') = \bar{\rho}\,\delta(\mathbf{r} - \mathbf{r}')$$

and the particle is completely localized, quite unlike what is indicated by the Bader criteria.

What we have found in this section is the delocalization indices based on the two-particle distribution when applied to a system of classical particles have a behavior that is completely contrary to the behavior of the sharing indices. According to the interpretations that have been given to λ(A) and δ(A,B), the former indices indicate that classical particles are not completely localized to a region, rather they are delocalized over macroscopic distances. The sharing index, on the other hand, shows complete localization in the classical limit.

V. Discussion and Summary

Several questions were raised in the Introduction. These included: (1) Is the behavior of the two-particle distribution function determined solely by the Pauli principle? (By "Pauli principle" we mean the general relation between spin and statistics.) (2) What is the role of the Fermi hole in determining the delocalization of an electron (or more generally of a particle)? (3) What single-particle properties can be determined solely from the two-particle distribution function? (4) Are there intrinsic differences between the Bader indices λ(A) and δ(A,B) and the sharing indices I_{AA} and B_{AB}? (5) What, if any, is the explanation for the rough agreement found between the values of the indices λ(A) and δ(A,B) and I_{AA} and B_{AB} found by Wang and Werstiuk?[8] (6) Do the Bader indices λ(A) and δ(A,B) in general give a measure of the delocalization of an electron? To these we add the questions: what can and what cannot the various indices determine?

The answers to these questions are predicated on the premise that any measure of the delocalization of a particle should be valid for any wave function and by inference for any state of the electrons, be it the ground electronic state, some excited electronic state, some state that is not an energy eigenstate, a general mixed (impure) state, or in the classical limit.

The answer to the first question is clear. That there are considerations beyond the Pauli principle that determine the two-particle distribution function was early recognized by Wigner and Seitz.[14] Specifically, these authors mentioned the correlation hole as "arising from the mutual repulsion terms, but they lie beyond the scope of Fock's equations." Beyond this, however, there are other considerations, such as mentioned in the Introduction; e.g., the location of a molecule relative to other molecules may be determined by the experimental setup.

The answer to the second question is answered, in part, by the considerations in section IV in which the Bader indices are considered for a mixture of ideal gases in a fixed volume behaving as a closed system and in part by the results of section III in which the Bader indices and the sharing indices are considered for simple, yet flexible, sets of wave functions describing fermionic and bosonic H_2. That the spatial point–point indices are precisely the same for a set of fermionic wave functions and bosonic wave functions is a strong argument that the Fermi hole in general does not determine the delocalization of a particle. In addition, in section IV a long-range contribution to the Bader index, δ(A,B), is found for ideal gas mixtures. Dilute gases composed of particles obeying either Fermi–Dirac or Bose–Einstein statistics behave ideally at high temperatures and both have the same two-particle distribution function. In this classical limit for which the thermal de Broglie wavelength Λ vanishes, there is no Fermi hole. A similar result holds for compressible fluids constrained as closed systems to a fixed volume. Again there is a long-range contribution to the Bader index, δ(A,B). We note that the sharing amplitude and the sharing index indicate complete localization of a particle in the limit of vanishing Λ.

The argument given in the Introduction gives the answer to question 3. There it was shown that in the absence of any other restriction, the only single-particle property that can be found solely from the two-particle distribution function is the one-particle density. Below we will note that there is a restriction that does allow certain other properties to be determined from the two-particle distribution function.

That there are intrinsic differences between the Bader indices λ(A) and δ(A,B) and the sharing indices I_{AA} and B_{AB} is clear from the contrast between the values of the indices for the same wave function when the mixing angle θ is negative. The underlying point–point indices have also been found to differ for almost all values of the mixing angle. The two exceptions are for $\theta = 0°$ and $\theta = 90°$, in which cases the wave function is a single determinant. Also found is a possible reason for the close agreement of the two sets of integrated indices found by

Wang and Werstiuk.[8] If the mixing of the approximate excited Hartree–Fock states into the lowest energy Hartree–Fock state to give a correlated ground-state wave function is of the form given for H_2 in the present paper for positive mixing angles, the term in the integrated indices that accounts for the differences may be small because of cancellations occurring in the integrals.

The analysis of the integrated indices in section III, proceeding directly from the underlying wave functions, indicate that the Bader indices do not give a measure of the delocalization of an electron whereas the sharing quantities do give a measure of the delocalization of an electron. For example, Table 1 gives the values of the indices for the singly excited state of H_2. The Bader delocalization index is found to be $\delta(\text{A,B}) = 1.791$ whereas the inter-basin sharing index is $B_{\text{AB}} = 0.209$. The latter, although nonzero, is in line with what is expected for a bond order arising from a single bonding orbital and a single antibonding orbital and with what is expected from the structure of the wave function, whereas the former is well out of line. (Parenthetically, we note that the sharing amplitude with the fixed point located on one of the protons does have a node between the fixed point and the other proton, this being indicative of an antibonding rather than a bonding situation.)

For this singly excited state, the integrated two-particle distribution functions are more amenable to direct interpretation than are the Bader indices, having the values of 0.896 and 0.104 for the self-index and inter-basin index, respectively. The interpretation is simply that if one particle is localized in the region of a given proton, the other particle is more likely to be in the region of that given proton.

In addition, the values of the indices, both the integrated indices and the point–point indices, are the same for the Fermi and for the Bose wave functions considered in this paper. This is a strong indication that the Fermi hole need have nothing to do with the localization of a single particle.

It is clear that the Bader indices and the sharing indices in general describe different aspects of the behaviors of electrons. What can be obtained from the two sets of indices? Are there ever some common features that can be obtained from the indices? What are the intrinsic differences between the sets of indices?

We first consider the properties of wave functions that are given by a single determinant. For such a wave function, the point–point indices $-F_N^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ and $I(\mathbf{r};\mathbf{r}')$ with the identifications $\mathbf{r}_1 = \mathbf{r}$ and $\mathbf{r}_2 = \mathbf{r}'$ have the same values and in this case the two sets of indices can, as indicated below, give common properties. Because the point–point sharing index has its source in the sharing amplitude $\langle\zeta;\zeta'\rangle$, because the one-particle density matrix $\rho_N(\zeta;\zeta')$ can be found from the amplitude by

$$\rho_N(\zeta;\zeta') = \int \langle\zeta;\zeta''\rangle \, \mathrm{d}\zeta'' \langle\zeta'';\zeta'\rangle$$

and because all the many-particle density matrixes can be expressed in terms of the single-particle density matrix when the wave function is a single determinant,[35] the sharing amplitude contains implicitly all properties of the system. In turn, the generalized (spin dependent) point–point Bader index is given by

$$F_N^{(2)}(\zeta_1,\zeta_2) = -\rho_N(\zeta_1;\zeta_2)\,\rho_N(\zeta_2;\zeta_1)$$

and if the single-particle density matrix can be unambiguously extracted from this, then all properties of the many-body system can be found from the point–point Bader index. In general, however, $\rho_N(\zeta;\zeta')$ is complex and it is not possible to carry out such an extraction unambiguously. If it is known that the one-particle density matrix is real and if the nodal surfaces can be identified (so that the positive and negative regions of $\rho_N(\zeta;\zeta')$ can be identified), all properties of the system can be found. Under such circumstances the two-particle distribution function is capable of giving the same information as the sharing amplitude, and in a sense the indices contain equivalent information.

When the wave function cannot be represented by a single determinant, the point–point sharing indices and the point–point Bader indices are nonequivalent. In such a case, what do and what do not the indices determine? Because the single-particle density matrix no longer determines the higher order density matrices, the single-particle sharing amplitude no longer determines the two-particle or any higher order distribution function. Only single-particle properties can be determined in general from the single-particle sharing amplitude. One of these properties is the extent of delocalization of a single particle. However, the single-particle quantities do not necessarily discriminate between different wave functions. Examples of such wave functions are given in this paper: the two wave functions $\Psi_{\text{FD},\theta}(\zeta_1,\zeta_2)$ and $\Psi_{\text{FD},-\theta}(\zeta_1,\zeta_2)$ give rise to the same single-particle sharing amplitude, and thus to the same point–point sharing index. On the other hand, the two-particle distribution function determines solely the behavior of a pair of particles and, concomitantly, the single-particle density. In general, it does not determine the delocalization of a single particle. However, the two-particle distribution function, and therefore the point–point Bader index, does discriminate between positive and negative values of the mixing angle for the wave functions given in this paper. (We do note that the single-particle amplitudes can be generalized to two-particle sharing amplitudes that not only distinguish between positive and negative values of the mixing angle but also distinguish between fermionic and bosonic behavior.) Lastly, the sharing quantities have a feature that is not inherent in quantities derived from the two-particle distribution function, the sharing amplitude. This amplitude in general has a rich nodal structure which, as illustrated in Figures 6 and 17, can be used to distinguish between different types of sharing, e.g., between bonding and antibonding types of sharing.

References and Notes

(1) Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391.

(2) Bader, R. F. W.; Johnson, S.; Tang, T.-H.; Popelier, P. L. A. *J. Phys. Chem.* **1996**, *100*, 15398.

(3) Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304.

(4) Molina, J. M.; Dobado, J. A.; Heard, G. L.; Bader, R. F. W.; Sundberg, M. R. *Theor. Chem. Acc.* **2001**, *105*, 365.

(5) Bader, R. F. W.; Bayles, D. *J. Phys. Chem. A* **2000**, *104*, 5579.

(6) Fradera, X.; Solà, M. *J. Comput. Chem.* **2002**, *23*, 1347.

(7) Matta, C. F.; Hernández-Trujillo, J.; Bader, R. F. W. *J. Phys. Chem. A* **2002**, *106*, 7369.

(8) Wang, Y.-G.; Werstiuk, N. H. *J. Comput. Chem.* **2003**, *24*, 379.

(9) Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397.

(10) Merino, G.; Vela, A.; Heine, T. *Chem. Rev.* **2005**, *105*, 3812–3841.

(11) Poater, J.; Duran, M.; Solà, M.; Silvi, B. *Chem. Rev.* **2005**, *105*, 3911–3947. It should be noted that in this review the differences are not ascribed to the differences in the qualities of the densities. Rather, the Fulton bond orders are considered as good approximations to the exact "delocalization indices".

(12) We follow Bader.[3]

(13) Reference 3, p 305.

(14) Wigner, E.; Seitz, F. *Phys. Rev.* **1934**, *44*, 509–524. The ideas were already in their earlier paper[15] and in: (a) Hylleraas, E. A. *Z. Phys.* **1928**, *48*, 469. (b) Bethe, H. *Z. Phys.* **1929**, *57*, 815.

(15) Wigner, E.; Seitz, F. *Phys. Rev.* **1933**, *43*, 804.

(16) Slater, J. C. *Rev. Mod. Phys.* **1934**, *6*, 209.

(17) Slater, J. C. *Phys. Rev.* **1951**, *81*, 385

(18) Maslen, V. W. *Proc. Phys. Soc. (London)* **1958**, *A69*, 734.

(19) McWeeny, R. *Rev. Mod. Phys.* **1960**, *32*, 335.

(20) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326.

(21) Fulton, R. L. *J. Phys. Chem.* **1993**, *97*, 7516.

(22) An indication that the derivation giving the connection of the two sets of indices given by Wang and Werstiuk[8] is incorrect is the following. Equation 8 of ref 8, on which the connection depends, is not the same as their eq 7. Rather the right-hand side of eq 8 is the absolute value squared of a particular sum of orbitals, $|(\sum_l n_l{}^{1/2}\eta_l(\mathbf{r}_1))|^2$, which in general is not the electron density.

(23) It should be noted that the pair density of Bader et al.[3] is $\rho_{\text{Bader}}(\mathbf{r}_1,\mathbf{r}_2) = {}^1/_2\sum_{\sigma_1,\sigma_2}\rho_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ in our notation.

(24) Bader[3] actually uses quantities which are integrated over atomic basins. These are simply found by integration of (6) over the appropriate atoms.

(25) In statistical mechanics $F_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ is the pair correlation function $h(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ multiplied by $\rho_N(\mathbf{r}_1\sigma_1)\ \rho_N(\mathbf{r}_2\sigma_2)$. See: Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford, New York, 1987; p 197. The correlation factor $f_N^{(2)}(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$ used by McWeeny[19] is $h(\mathbf{r}_1\sigma_1,\mathbf{r}_2\sigma_2)$.

(26) The sharing indices and the two-particle distribution function for this model were analyzed in part by: Fulton, R. L.; Mixon, S. T. *J. Phys. Chem.* **1995**, *99*, 9768.

(27) Bader, R. F. W.; Tal, Y.; Anderson, S. G.; Nguyen-Dang, T. T. *Isr. J. Chem.* **1980**, *19*, 8.

(28) While the manuscript was under review, the following paper appeared: Matito, E.; Duran, M.; Solà, M. *J. Chem. Educ.* **2006**, *83*, 1243. The expressions for λ(A) and δ(A,B) are the same as eq 1.6 of that paper. The paper also gives values of λ(A) and δ(A,B) for a discrete set of values of the mixing angle ranging from 0 to $\pi/4$ using results of calculations done at the STO-3G level of approximation.

(29) Weinbaum, S. *J. Chem. Phys.* **1933**, *1*, 593.

(30) Fradera and Solà give ${}^1\delta_3(\text{A,B}) = 1$ in Appendix A of ref 6 and state that for the three singlet wave functions considered, the ground state, the doubly excited state, and the singly excited wave functions, the electrons are not correlated. The first two states are given by single determinant wave functions; however, the third is not. The particles in the singly excited state are, in fact, correlated. If particle 1 is described by the function $\varphi_s(\mathbf{r}_1)$, particle 2 is of necessity described by the function $\varphi_a(\mathbf{r}_2)$ and vice versa.

(31) Rincón, L.: Alvarellos, J. E.; Almeida, R. *J. Chem. Phys.* **2005**, *122*, 214103. Figure 1 of this reference gives the values of $-n_{\text{XC}}(\mathbf{r}_1,\mathbf{r}_2)$ along the internuclear axis when the reference electron at $\mathbf{r}_1$ is at the location of one of the protons. When multiplied by the electron density $\rho(\mathbf{r}_1)$, this is the point−point Bader index, the result being a subset of the points plotted in Figure 8.

(32) Hill, T. L. *Statistical Mechanics*; Dover: New York, 1987; p 84.

(33) Reference 32, pp 407ff. To the best of my knowledge the connection was originally given in the thesis of: de Boer, J. *Contribution to the Theory of Compressed Gases*; H. J. Paris: Amsterdam, 1940; p 83.

(34) In the limit that $h \rightarrow 0$, $(8\pi mkT/h^2)^{3/4}e^{-mkT(\mathbf{r}-\mathbf{r}')^2/\hbar^2}$ vanishes when $(\mathbf{r}-\mathbf{r}')^2 \neq 0$ and is infinite when $(\mathbf{r}-\mathbf{r}')^2 = 0$. It represents a square root of the Dirac δ-function such that $[\sqrt{\delta(\mathbf{r}-\mathbf{r}')}\,]^2 = \delta(\mathbf{r}-\mathbf{r}')$. Unlike the δ-function, the integral of $\sqrt{\delta(\mathbf{r}-\mathbf{r}')}$ over $\mathbf{r}'$ vanishes. The density matrix, $\rho(\mathbf{r};\mathbf{r}') = \bar{\rho}\exp[-mkT(\mathbf{r}-\mathbf{r}')^2/2\hbar^2]$, is also short ranged. In the limit that $h \rightarrow 0$, $\rho(\mathbf{r};\mathbf{r}')$ vanishes when $(\mathbf{r}-\mathbf{r}')^2 \neq 0$ and equals $\bar{\rho}$ when $(\mathbf{r}-\mathbf{r}')^2 = 0$.

(35) Dirac, P. A. M. *Proc. Camb. Philos. Soc.* **1931**, *27*, 240.