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Proton Spin−Spin Coupling and Electron Delocalization

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The spin−spin coupling of protons measured by the constant $J_{HH'}$ in NMR experiments is dominated by a term proportional to the product of the electron spin densities at the two nuclei, the Fermi contact term. The probability of β electrons being in excess over α electrons at the position of nucleus $\mathbf{n}'$, given that there is an α electron at $\mathbf{n}$, is proportional to the negative of the exchange density, the total Fermi correlation between $\mathbf{n}$ and $\mathbf{n}'$. Thus the delocalization of the Fermi hole between $\mathbf{n}$ and $\mathbf{n}'$ is the mechanism whereby the spin perturbation caused by the magnetic interaction of an electron with nucleus $\mathbf{n}$ is transmitted to $\mathbf{n}'$. The density and exchange density within the basin of a hydrogen atom are described primarily in terms of s-type basis functions, and one may approximate the exchange density between two protons at $\mathbf{n}$ and $\mathbf{n}'$ by the exchange between the two associated atomic basins determined by the delocalization index δ(A,B) within the quantum theory of atoms in molecules. It is shown that this model yields good linear regression equations relating $J_{HH'}$ to δ(H,H′) for hydrogen atoms bonded to different carbons in alkanes, alkenes, their cyclic congeners, and polybenzenoid hydrocarbons.

Delocalization of Electrons

Electron delocalization has long been invoked to rationalize problems of structural stability and chemical reactivity, particularly in conjugated and aromatic molecules. These discussions were understandably couched initially in terms of the orbital model,[1,2] an early example of prime importance being Coulson's use of molecular orbital theory to define a bond order.[3−5] His definition of a mobile bond order, as determined by the delocalization of electrons between a pair of bonded atoms, referred to delocalized π electrons and involved a summation of products of coefficients of atom-centered basis functions over the π molecular orbitals. Such a definition that relates delocalization to a property determined by all of the occupied orbitals is to be contrasted with the subsequent introduction of localized orbitals and their use in discussions of electron localization. In this model, the spatial localization/delocalization of individual pairs of electrons is related to the corresponding property of an individual molecular orbital. In fact, all orbitals contribute to the pair density, the density that determines electron localization. The pair density, like the one-electron density, is invariant to any unitary transformation of the orbitals, and no individual orbital can be identified as determining any observable feature of a molecule, the use of Koopman's theorem to approximate an ionization potential in terms of a canonical orbital energy being a notable exception. With the advent of modern computational facilities, the need for the use of models in the description of electron delocalization is obviated, and instead, one may use quantum mechanics to obtain a definition of electron delocalization and determine its effect on measurable properties of a system.

Salem[1] noted that Coulson's definition of a mobile bond order[2] in the molecular orbital theory of conjugated systems serves as a link between Fermi correlation and electron delocalization. In 1975, Bader and Stephens,[6] showed that the spatial pairing of electrons and their localization is a consequence of the Fermi correlation determined by the electron pair density. They demonstrated that the extent to which electrons are spatially localized or delocalized is determined by the corresponding spatial extent of the density of the Fermi hole, as measured by the exchange of same-spin electrons. It has since been proposed[7] that the spatial distribution of the Fermi correlation be used to provide a common, quantitative basis for the concept of electron delocalization, as it is used throughout chemistry, a conclusion supported by a recent study wherein the same correlation was used to account for the patterns of delocalization that account for the spectroscopic and reactive properties of the polybenzenoid hydrocarbons.[8] Most importantly, it was demonstrated[7] that Fermi correlation can be considered to be the mechanism whereby distant atoms communicate with one another. This is exemplified further in the present paper by showing how the delocalization of the spin density between the basins of different hydrogen atoms provides a model for the understanding of measured long-range proton spin−spin coupling constants, constants that do not necessarily exhibit a simple falloff with increasing internuclear separation.

Electron Delocalization and Fermi Correlation

The Fermi hole, the physical manifestation of Pauli's exclusion principle, has a simple physical interpretation:[6] it provides 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

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the presence of an identical amount of same-spin density.[9] It is a negative quantity, because it decreases the amount of same-spin density throughout space by one electronic charge. If the density of the Fermi hole is maximally localized in the vicinity of the reference point, then all other same-spin electrons are excluded from its vicinity and the reference electron is localized. For a closed-shell molecule, the result is a localized α,β pair. Correspondingly, the electron can go wherever its Fermi hole goes, and if the Fermi hole of an electron when referenced to a given atom is delocalized into the basin of a second atom, then the electron is shared between them.

While the ideas developed here apply to any level of theory, the discussion is given in terms of the Hartree−Fock (H−F) model. Not only is Fermi correlation the sole source of electron correlation in the H−F model of electronic structure, but the H−F description is acknowledged to provide an excellent approximation to this quantity. The density of $\alpha-\beta$ pairs is uncorrelated in H−F and is given by the simple product of the corresponding spin densities

$$\rho^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) = \rho^{\alpha}(\mathbf{r}_1)\rho^{\beta}(\mathbf{r}_2) \tag{1}$$

The pair density for same-spin electrons is however, mediated by the density of the Fermi hole, $h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2)$, and given by

$$\rho^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = \rho^{\alpha}(\mathbf{r}_1)\{\rho^{\alpha}(\mathbf{r}_2) + h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2)\} \tag{2}$$

where the density of the Fermi hole for electrons of α spin is given by

$$h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) = -\sum_i\sum_j\{\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\}/\rho^{\alpha}(\mathbf{r}_1) \tag{3}$$

and the sums run over the α spin orbitals. This density exhibits the required properties of reducing to $-\rho^{\alpha}(\mathbf{r}_1)$ when $\mathbf{r}_2 = \mathbf{r}_1$, corresponding to the complete removal of same-spin density from the position of the reference electron and yielding −1 when integrated over the space of the second electron, demonstrating that the Fermi hole associated with a given electron removes the equivalent of one electronic charge. The quantity in curly brackets in eq 2 is the conditional same-spin density, the probability of an α electron being at $\mathbf{r}_2$ when another is at $\mathbf{r}_1$. Because $h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) < 0$, the role of the Fermi hole is to decrease the α spin density at $\mathbf{r}_2$ by an amount determined by the extent of the delocalization of the Fermi hole away from $\mathbf{r}_1$.

One sees from eq 3 that the product $\rho^{\alpha}(\mathbf{r}_1)h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2)$ equals the H−F exchange density. When this product is integrated over the coordinates of both electrons, it yields $-N^{\alpha}$, the negative of the total number of α electrons, that is, the total Fermi correlation for electrons of α spin. Thus, the double integration of this product over some region A, a quantity denoted by $F^{\alpha}(\mathrm{A,A})$ in eq 4, yields the total Fermi correlation for the α electrons in the region A,[6]

$$F^{\alpha}(\mathrm{A,A}) = \int_{\mathrm{A}} d\mathbf{r}_1 \int_{\mathrm{A}} d\mathbf{r}_2\, \rho^{\alpha}(\mathbf{r}_1)h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) \tag{4}$$

Its limiting value is $-N^{\alpha}(\mathrm{A})$, the negative of the α spin population of region A, a value that would correspond to the electrons in A being totally localized to this region because all remaining α spin density would then be excluded from A. The limiting value implies that the electrons in A do not exchange with electrons outside of A, that is, they would be totally localized within A. The magnitude of $(|F^{\alpha}(\mathrm{A,A})| + |F^{\beta}(\mathrm{A,A})|)$ is termed the *localization index*, $\lambda(\mathrm{A})$.

The limit of total localization, while approached quite closely (≥95%) in ionic systems, can never be attained, and one finds that $|F^{\alpha}(\mathrm{A,A})| < N^{\alpha}(\mathrm{A})$, indicating that the electrons in region A exchange with electrons outside the boundaries of A, that is, they are delocalized. The delocalization of the electrons from a region A into another region B is determined by the quantity $F^{\alpha}(\mathrm{A,B})$, eq 5,[6]

$$F^{\alpha}(\mathrm{A,B}) = \int_{\mathrm{A}} d\mathbf{r}_1 \int_{\mathrm{B}} d\mathbf{r}_2\, \rho^{\alpha}(\mathbf{r}_1)h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2) \tag{5}$$

One necessarily has $F^{\alpha}(\mathrm{A,B}) = F^{\alpha}(\mathrm{B,A})$ and the exchange of electrons between the two regions—the delocalization of the electrons between the two regions—is given by the delocalization index $\delta(\mathrm{A,B}) = 2|F^{\alpha}(\mathrm{A,B})| + 2|F^{\beta}(\mathrm{A,B})|$.[10]

The integrals $F^{\alpha}(\mathrm{A,A})$ and $F^{\alpha}(\mathrm{A,B})$ determining the localization and delocalization of electrons, respectively, are obtained by the corresponding double integrations of the Hartree−Fock exchange density, as illustrated in eq 6 for $F^{\alpha}(\mathrm{A,B})$,

$$F^{\alpha}(\mathrm{A,B}) = -\sum_i\sum_j\int_{\mathrm{A}} d\mathbf{r}_1 \int_{\mathrm{B}} d\mathbf{r}_2 \{\phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\} = -\sum_i\sum_j S_{ij}(\mathrm{A})S_{ji}(\mathrm{B}) \tag{6}$$

The second-order density matrix obtained from a CI calculation can also be expressed in terms of products of basis functions multiplied by the appropriate coefficients enabling one to express the integrated pair density in terms of overlap contributions. Thus, terms similar to those in eq 6 multiplied by the appropriate coefficients appear in the CI expression for $F^{\alpha}(\mathrm{A,B})$, and delocalization is still described in terms of the exchange of electrons between molecular orbitals in a wave function that includes Coulomb, as well as Fermi, correlation.[10]

The above ideas, when used in conjunction with the quantum theory of atoms in molecules (QTAIM),[11] enable one to determine the extent to which electrons are localized within the basin of a given atom or delocalized into the basin of a second atom. QTAIM defines an atom as an open system bounded by a surface of local zero flux in the gradient vector field of the electron density. An electron population is, like all properties, defined as the expectation value of a corresponding observable, in this case the number operator for electrons of either spin. Because the Fermi correlation counts all of the electrons, the localization and delocalization indices sum to N and they provide a quantitative measure of how the N electrons in a molecule are localized within the individual atomic basins and delocalized between them.

The delocalization index for a pair of bonded atoms—atoms the nuclei of which are linked by a bond path[12]—exhibits the properties associated with a Lewis bond order.[10,13] For a pair of identical bonded atoms or one with small interatomic charge transfer, its value equals the number of electron pairs shared between the two atomic basins: 1.0 for H_2; 3.0 for N_2; 0.99 and 0.97 for CC and CH in saturated hydrocarbon; 1.9 and 0.98 for the same atomic pairs in ethylene. The values for a polyatomic molecule are invariably somewhat less than the limiting integer values because of the delocalization of density into the basins of other atoms linked to the pair in question. Theory provides a precise determination of bonding—two atoms being bonded if their nuclei are linked by a bond path.[12] Hence, the $\delta(\mathrm{A,B})$ will not be referred to as a bond order in the general case, because electrons are delocalized between all pairs of atoms in a molecule.

There is close connection between Coulson's mobile bond order and Fermi correlation, as described in Salem's book on molecular orbital theory of conjugated systems.[1] Within this theory, atomic charges and bond orders are determined by the products of coefficients of the carbon atomic π orbitals (AOs) obtained when a given MO is squared to obtain an expression for its density, the products of the AOs themselves being equated to unity. A product of coefficients is identified with an atomic charge when both AOs refer to the same atom and with a bond order when they are on different carbons. When these products are summed over all MOs, one obtains q_r, the atomic charge for atom r, and p_{rs}, the mobile bond order for atoms r and s. Using this formalism, we reduce the same-spin pair density, eq 2, to

$$\rho^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) = (^1/_4)\{q_r q_s - p_{rs}^{\;2}\} \tag{7}$$

which is to be compared with eq 2. To quote Salem "The square of the bond order between atoms r and s represents the extent of the *total* (Fermi) *correlation between the two electrons with parallel spin*, one at r, the other at s.", that is, it equals the exchange of electrons between r and s. This expression of the Fermi correlation has been used by McConnell to account for the long-range spin−spin coupling between protons.[1,14]

Proton Spin-Spin Coupling and Electron Exchange

The older literature argued that the spin−spin coupling of protons should be dominated by the product of the Fermi contact terms for the two nuclei,[15,16] a view that is substantiated in the modern literature. Wilkens et al.,[17] in the calculation and analysis of the angular and distance dependence of the vicinal proton spin couplings in ethane and of the long range couplings in pentane, treat only the Fermi contribution noting that "previous work (as referenced in their paper) strongly suggests that the Fermi contact mechanism dominates." The spin magnetic moment of a proton polarizes the spin density of the electrons in its immediate vicinity, resulting in a small excess of oppositely polarized electron spin density. This information is transmitted to the vicinity of a second proton via the mechanism of electron exchange. If one interprets the pair density as a pair probability distribution and denotes the position coordinates of two protons by **n** and **n′**, then $\rho^{\alpha\beta}(\mathbf{n},\mathbf{n}')$, the probability of an α electron being at **n** and a β electron at **n′**, is given by the (uncorrelated) product $\rho^{\alpha}(\mathbf{n})\rho^{\beta}(\mathbf{n}')$. However, $\rho^{\alpha\alpha}(\mathbf{n},\mathbf{n}')$, the probability of an α electron being at **n** when another α electron is at **n′** is mediated by the density of the Fermi hole and is given by $\rho^{\alpha}(\mathbf{n})\rho^{\alpha}(\mathbf{n}') + \rho^{\alpha}(\mathbf{n})h^{\alpha}(\mathbf{n},\mathbf{n}')$, eq 2. For a closed-shell system, $\rho^{\alpha}(\mathbf{r}) = \rho^{\beta}(\mathbf{r})$ and the difference $\rho^{\alpha\beta}(\mathbf{n},\mathbf{n}') - \rho^{\alpha\alpha}(\mathbf{n},\mathbf{n}')$ reduces to minus the exchange density, the quantity $-\rho^{\alpha}(\mathbf{n})h^{\alpha}(\mathbf{n},\mathbf{n}')$. Thus, the probability of β electrons being in excess over α electrons at the position of nucleus **n′**, given that there is an α electron at **n**, is proportional to the negative of the exchange density. The density of α spin electrons at nucleus **n′** is lessened to the extent that the density of the Fermi hole extends from the reference nucleus **n** to **n′**, and this is the mechanism whereby the spin perturbation caused by the magnetic interaction of an electron with nucleus **n** is transmitted to **n′**.[7]

McConnell showed that the same conclusion regarding the proportionality between the excess of β over α spins and exchange can be obtained from the second-order perturbation expression for the coupling of nuclear spins via the electron spin.[14] There are three contributions to the Hamiltonian describing the perturbations arising from a magnetic nucleus interacting with the spin magnetic moment of an electron:[18] one involving the motion of the electrons in the magnetic field of the nuclei, another representing the dipole−dipole interaction between the nuclear and electronic and magnetic moments, and third, that arising from the coupling of the nuclear spins via the spin of the electrons. It is this latter term that dominates the spin−spin coupling of protons. It is determined by the product of matrix elements for the operator $\mathbf{S}_k\cdot\mathbf{I}_n$, the operators for the electronic and nuclear spin, a contribution that reduces to the product of the Fermi contact terms for the two nuclei in question. The matrix elements mix the singlet ground state with triplet excited states in the second-order expression for the energy of interaction. If one makes the approximation of replacing all of the triplet excitation energies by a mean value, ΔE, then the perturbation expression reduces to the averaging of terms involving the operators $\mathbf{S}_j\cdot\mathbf{S}_k\delta(\mathbf{r}_{jn})\delta(\mathbf{r}_{kn'})$, products of the electronic spin operators mediated by the term giving the product of electron densities at the positions of the two nuclei **n** and **n′**, averaged over the ground-state wave function. (The symbol $\delta(\mathbf{r}_{jn})$ used by McConnell is an abbreviation of the Dirac delta operator $\delta(\mathbf{r}_j - \mathbf{X}_n)$, where $\mathbf{X}_n$ is the coordinate of nucleus **n**).

It is the averaging of this operator over the coordinates of all j,k pairs of electrons for the ground-state wave function that yields an expression for the spin−spin coupling constant $J_{nn'}$ that is proportional to the negative of the exchange density. Specifically, the expression for the coupling constant in standard notation[18] becomes

$$J_{nn'} = -\frac{2}{3h}\left(\frac{16\pi\beta\hbar}{3}\right)^2 \gamma_N\gamma_{N'}\frac{1}{\Delta E}\sum_i\sum_j\langle\phi_i(\mathbf{r}_1)\delta(\mathbf{r}_{1n})\phi_j(\mathbf{r}_1)\rangle \langle\phi_j(\mathbf{r}_2)\delta(\mathbf{r}_{2n'})\phi_i(\mathbf{r}_2)\rangle \tag{8}$$

Equation 8 states that $J_{nn'}$ is proportional to the product of densities at the two nuclei that arise from the exchange of same-spin electrons. This general expression was first obtained by McConnell[14] who pointed out that if one considers each proton to be described by a 1s orbital, then the exchange term appearing in eq 8 reduces, as shown in eq 7, to a term proportional to Coulson's mobile bond order[4,5] between nonbonded hydrogen atoms multiplied by the product of spin densities at the two protons.

The dominance of the Fermi contact contribution to $J_{HH'}$ for nonbonded hydrogens is primarily a consequence of 1s-like functions dominating the basis set for the hydrogen atoms. It is therefore, reasonable to assume that the density at a proton should parallel the increase in the density within the basin of a hydrogen atom, enabling one to make the identification

$$\langle\phi_i(\mathbf{r}_1)\delta(\mathbf{r}_{1n})\phi_j(\mathbf{r}_1)\rangle\langle\phi_j(\mathbf{r}_2)\delta(\mathbf{r}_{2n'})\phi_i(\mathbf{r}_2)\rangle \rightarrow \langle\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\rangle_H\langle\phi_j(\mathbf{r}_2)\phi_i(\mathbf{r}_2)\rangle_{H'} = S_{ji}(H)S_{ij}(H') \tag{9}$$

wherein one replaces the exchange density at the positions of the protons **n** and **n′** with its integration over the respective atomic basins H and H′. Hence, the double sum appearing in the expression for the coupling constant in eq 8 reduces, with a change in sign, to eq 6, the expression for $|F^{\alpha}(H,H')| + |F^{\beta}(H,H')| = \delta(H,H')/2$, one-half the delocalization index that measures the exchange of electrons between the two atomic basins. Thus one is led to propose that the coupling constant between the protons of nonbonded hydrogen atoms H and H′, be proportional to the delocalization index $\delta(H,H')$. This proportionality is not expected to apply to atoms other than hydrogen because the presence of basis functions with nonzero angular momentum in a primary rather than a polarizing role for non-hydrogenic atoms increases the contributions of the other two coupling contributions relative to the Fermi contact term in the determination of $J_{nn'}$. The higher angular momentum basis functions also destroy the assumed proportionality between the atomic integration of the exchange density and its value at the nucleus of the atom.

One of the most striking features of proton spin−spin coupling is the relatively small values found for protons bonded to the same carbon atom, a result not recovered by the delocalization indices. The small values are attributed to the nodal properties of a pair of C−H bonding orbitals on one carbon exhibiting planes in the proximity of the protons bonded to the same carbon,[18] thus negating the proportionality between the integrated atomic exchange density and its value at a proton. This interorbital nodal effect is not found for hydrogens bonded to adjacent or more widely separated carbons.

Correlation of δ(H,H′) with $J_{HH'}$

It was previously demonstrated[7] that the delocalization index for the vicinal protons in ethane yield an excellent correlation with their coupling constants as a function of the torsion angle about the C−C axis predicted by the Karplus equation.[19] In the present work, we compare the correlation of δ(H,H′) with measured coupling constants for hydrogen atoms bonded to different carbon atoms in alkanes, alkenes, their cyclic congeners, and polybenzenoid hydrocarbons. An interesting feature of the measured constants $J_{HH'}$ is that they can be largest for protons that are separated by the greatest distance, a feature faithfully recovered by the corresponding values of δ(H,H′).

The dominance of the Fermi contact (FC) contribution in these particular molecules is demonstrated by data supplied by one of the referees of this paper, who calculated all three contributions to $J_{HH'}$ for the couplings in naphthalene using the de Mon NMR code with the Perdew−Wang exchange and the Perdew correlation using a QZ2P quality basis set. The results show that the Fermi contribution closely parallels both the experimental and calculated $J_{HH'}$ values, the two sets of $J_{HH'}$ values being in good agreement with one another. While the two remaining contributions, the diamagnetic and paramagnetic spin−orbit (SO) terms are separately not zero, they are of opposite sign and of almost equal magnitude with the net result that their net contribution is nearly zero and $J_{HH'}$ is determined in its essential entirety by the FC contribution. With the data supplied by the referee, the FC contribution yields a linear regression with the experimental $J_{HH'}$ values with $r^2 = 0.995$ and another with the calculated values with $r^2 = 1.000$. Neither of the SO terms correlate in any way with the calculated or experimental $J_{HH'}$. As examples of the SO contributions, we quote the paramagnetic and diamagnetic values in hertz for the largest and the smallest couplings, together with the calculated $J_{HH'}$ value: for H1H2, the values are 0.11 and −0.35 to give a net SO contribution of −0.24 or 3% of $J_{HH'} = 7.92$; for H2H7, the values are 0.94 and −0.95 to give net SO contribution of −0.01 or 3% of $J_{HH'} = 0.19$. Thus, because of the near cancellation of the SO contributions, the FC term accounts for 97% of the coupling in each case.

The delocalization indices between the carbon atoms in the polybenzenoid hydrocarbons listed in Table 1 were determined to obtain a measure of the effect of ring fusion on the uniform delocalization of the π electrons found in benzene and thereby obtain a measure of the aromaticity in these molecules.[8] The fusion of one or more benzenoid rings results in the delocalization of electrons increasing between certain pairs of bonded carbon atoms and decreasing between others, relative to that found in benzene. For example, the value of 1.39 for δ(C,C′) in benzene increases to 1.63 for the unique 9−10 bond in phenanthrene (compared to a value of 1.89 for the CC bond in ethylene), while the values for the neighboring CC bonds decrease to 1.14. Thus, the hydrogens in these molecules are bonded to a carbon framework that exhibits bond orders lying between those for single and double bonds.

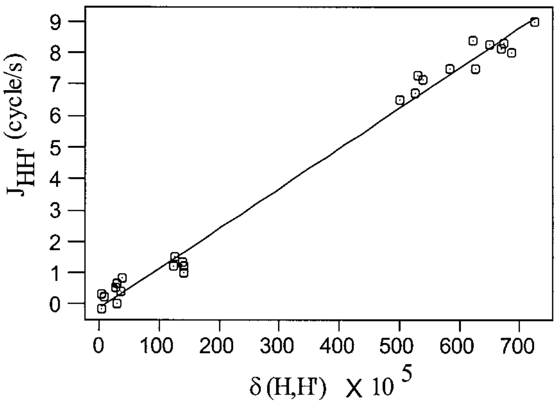

Figure 1. A scatter plot of the hydrogen−hydrogen delocalization indices, δ(H,H′), versus the proton−proton NMR spin−spin coupling expressed in cycles/sec (Hz) in polybenzenoid hydrocarbons showing a strong linear relationships. Data corresponding to this plot are listed in Table 1.

The wave functions for the polybenzenoids were obtained at the restricted Hartree−Fock (RHF)/6-31G**//6-31G** level using Gaussian 94,[20] as were the wave functions for the other molecules considered in this work. The atomic integrations were obtained using AIMPAC[21] and the delocalization indices from AIMDELOC.[22]

It is found that the values of δ(H,H′) yield a linear statistical correlation with the measured $J_{HH'}$ coupling constants displayed in Figure 1 given in the regression eq 10

$$J_{HH'} = -0.1369 + 1275\delta(\mathrm{H,H'}) \tag{10}$$

with $r^2 = 0.989$ and a sample estimate of the standard deviation $(\sigma) = 0.375$. The values of δ(H,H′) have been previously shown to be relatively insensitive to the basis set providing polarization functions are included.[10] To test whether the correlation holds for a much larger basis set in the case of polybenzenoid hydrocarbons, the calculations were repeated for benzene and naphthalene at the RHF/6-311++G(2d,2p)//6-311++G(2d,2p) level and were found to yield an even better linear regression with $r^2 = 0.990$ and $\sigma = 0.335$. Moreover, the set of 12 δ(H,H′) values obtained with the large basis set was found to differ by an average absolute deviation of 9×10^{-5} from the corresponding set calculated with the 6-31G** basis set, a difference too little to have any physical significance. The values of δ(H,H′) calculated using the larger basis set are included in Table 1.

The experimental values are grouped into two sets: those from 7 to 9 Hz for protons separated by three bonds and those from 2 Hz extending down to and past zero for protons with greater interbond separations. A negative coupling constant implies that the two protons that are coupled have the same spin. While three negative values of $J_{HH'}$ are obtained from the correlation compared to the single experimental example, all three are for couplings that are close to zero.

One notes that both the experimental and theoretical values for the 1−5 coupling in naphthalene are greater than those for 1−4, even though the 1−5 internuclear separation exceeds that for 1−4. Similarly, the 1−5 coupling is greater than the 1−6 coupling, although the former pair of protons are separated by seven bonds, the latter pair by six. The δ(H,H′) values become quite small for the long-range couplings and approach the limits of the integration errors of the orbital overlaps over the atomic basins that are required for their evaluation. The total Fermi correlation, because it accounts for the removal of N electrons,

TABLE 1: $J_{\mathrm{H,H'}}$ Coupling Constants in Some Aromatic Molecules in Hz[a]

	H	H′	$\delta(\mathrm{H,H'}) \times 10^5$	$J_{\mathrm{H,H'}}$ calcd	$J_{\mathrm{H,H'\,av}}$ exptl	σ	n	ref
benzene	1	2	585 (561)	7.32	7.51	0.03	5	28
benzene	1	3	139 (138)	1.64	1.34	0.03	5	28
benzene	1	4	30 (41)	0.25	0.66	0.03	5	28
naphthalene	1	2	650 (630)	8.14	8.28	0.19	4	28
naphthalene	1	3	136 (134)	1.60	1.24	0.11	4	28
naphthalene	1	4	30 (39)	0.24	0.00		1	28
naphthalene	1	5	38 (37)	0.35	0.83		1	28
naphthalene	1	6	4 (4)	−0.09	−0.16		1	28
naphthalene	1	7	8 (9)	−0.03	0.21		1	28
naphthalene	2	3	526 (496)	6.57	6.71	0.19	4	28
naphthalene	2	4	136 (134)	1.60	1.24	0.11	4	28
naphthalene	2	6	5 (9)	−0.07	0.28		1	28
anthracene	1	2	674	8.46	8.30		1	28
anthracene	1	3	135	1.59	1.20		1	28
anthracene	2	3	501	6.25	6.50		1	28
phenanthrene	1	2	623	7.81	8.42	0.17	3	28
phenanthrene	1	3	141	1.66	1.21	0.28	3	28
phenanthrene	1	4	28	0.22	0.58	0.06	3	28
phenanthrene	2	3	539	6.74	7.13	0.21	3	28
phenanthrene	2	4	127	1.48	1.50	0.09	3	28
phenanthrene	3	4	670	8.40	8.14	0.23	3	28
phenanthrene	4	10	36	0.32	0.40		1	29
chrysene	1	2	686	8.61	8.00		1	30
chrysene	1	3	125	1.45	1.20		1	30
chrysene	1	4	29	0.23	0.50		1	30
chrysene	2	3	531	6.64	7.30		1	30
chrysene	2	4	142	1.67	1.00		1	30
chrysene	3	4	627	7.86	7.50		1	30
chrysene	5	6	726	9.12	9.00		1	30

[a] The columns labeled H and H′ list the standard numbering of the carbon atom to which the hydrogen atom in question is bonded. The column labeled $\delta(\mathrm{H,H'})$ lists the value of the delocalization indices for the 6-31G** calculations. The values in parentheses are for the 6-311++G(2d,2p) calculations. The column labeled $J_{\mathrm{H,H'}}$ lists the calculated spin−spin coupling constants obtained from the regression equation (eq 10). The column labeled $J_{\mathrm{H,H'\,av}}$ provides the experimental value of the coupling between the two hydrogen atoms. Entries under $J_{\mathrm{H,H'\,av}}$ are average values reported by n authors and collected in ref 28. The standard deviation of each set of n reported values is given in the column labeled σ. The limits of accuracy of the data as measured by $(|\Delta)|/N) \times 10^5$ and that is defined in the text is 33.6 for benzene, 20.3 for naphthalene, 16.9 for anthracene, 5.0 for phenanthrene, and 1.8 for chrysene.

TABLE 2: $J_{\mathrm{H,H'}}$ Coupling Constants in Some Saturated Molecules

	atom label	$\delta(\mathrm{H,H'}) \times 10^5$	$J_{\mathrm{H,H'}}$ calcd	$J_{\mathrm{H,H'}}$ exptl	ref
ethane (staggered)	av[a]	657	9.7	8[b]	31
cyclohexane	a−a	1173	13.4	13.2	31
cyclohexane	a−e	446	4.6	3.6	31
cyclohexane	e−e	360	3.6	3.1	31
cyclohexene	av[c]	304	2.9	3.1	32
1,3-cyclohexadiene	*d*	419	4.3	5.1	33

[a] Average value taken over the two gauche vicinal hydrogen atoms (±60°) and the trans vicinal hydrogen (180°). [b] Datum not used to obtain the regression equation. [c] Average values for $J_{\mathrm{H,H'}}$ and for $\delta(\mathrm{H,H'})$ taken between the hydrogen atom bonded to carbon C2 (IUPAC numbering) and the two nonequivalent vicinal hydrogen atoms bonded to the saturated carbon C3. Symmetry equivalents are C1 and C4, respectively. [d] Values for vicinal hydrogen atoms separated by the single bond within the conjugated part of the molecule (i.e., C2 and C3, IUPAC numbering).

sums to $-N$. Thus, the sum of the localization indices over all of the atoms and one-half of the delocalization indices over all pairs of atoms should yield N, thereby providing a measure of the accuracy of the atomic overlap integrations. The footnote to Table 1 includes the magnitude of the differences (Δ) between N and the sum of the indices divided by N for the studied molecules. Thus for benzene, the 1−4 index, which equals 0.0003, equals the average error per electronic charge incurred in the integrations.

While the correlation between $\delta(\mathrm{H,H'})$ and $J_{\mathrm{HH'}}$ is less faithful for protons separated by more than three bonds, one notes that both $J_{\mathrm{HH'}}$ and $\delta(\mathrm{H,H'})$ decrease in parallel for the small couplings, decreases that are not simply related to increases in the degree of separation of the protons. Thus, the essential physics is recovered in the $\delta(\mathrm{H,H'})$ values, even though the correlation is no longer as exact.

An even more striking example of the inverse correlation of $J_{\mathrm{HH'}}$ with the separation between vicinal protons is found for the cis and trans proton couplings in ethylene for which the trans coupling is nearly twice that of the cis. Experimentally, the values for variously substituted ethylenic molecules fall in the ranges of 17−18 and 8−11 Hz for the trans and cis coupling, respectively,[18] while eq 10 yields corresponding values of 16.2 and 9.7 Hz, values that are bracketed by the experimental ones. Experimental $J_{\mathrm{HH'}}$ constants for the vicinal protons linked by a carbon−carbon double bond are known for both cyclohexene, 8.8 Hz, and 1,3-cyclohexadiene, 9.4 Hz, while those predicted using eq 10 are 10.5 and 9.3 Hz, respectively.

The possibility of the π system contributing to the coupling of aromatic protons via the mechanism of configuration interaction is considered to be relatively small.[18] McConnell[23] has estimated the π contribution to the coupling between the ortho protons in benzene to be 0.80 Hz. The ability to linearly relate the coupling constants to the $\delta(\mathrm{H,H'})$ values further speaks to the relative nonimportance of the π contribution to the coupling, because there is no exchange between the σ and π electrons and the π orbitals make no direct contribution to the hydrogen delocalization indices.

The proton spin−spin coupling constants for vicinal hydrogens in saturated hydrocarbons correlate equally well with the delocalization index, although they require a separate regression equation, eq 11

$$J_{\mathrm{HH'}} = -0.8143 + 1191\delta(\mathrm{H,H'}) \tag{11}$$

Equation 11, with $r^2 = 0.975$ and $\sigma = 0.793$, was fitted to $J_{\mathrm{HH'}}$ values for the vicinal hydrogens listed in Table 2, excluding the averaged value for ethane. The magnitude of $J_{\mathrm{HH'}}$ in saturated hydrocarbons can also exhibit the property of increasing with increasing internuclear separation, as exemplified by the coupling between the trans protons in staggered ethane predicted to be 15.5 cycles/sec compared to 5.3 cycles/sec for the gauche pair, a trend also predicted by the Karplus equation.[19] Similarly, the axial−axial coupling of neighboring protons in cyclohexane that are trans related is greater than that for the axial−equatorial- or equatorial−equatorial-related pairs the internuclear separations of which decrease in the same order. These variations are faithfully recovered by the relative values of the corresponding $\delta(\mathrm{H,H'})$ indices, Table 2. The semiquantitative success of the correlations obtained with eqs 10 and 11 speaks not only to the physical soundness of the underlying model that relates the Fermi contact terms to electron delocalization but also to the ability of the quantum definition of an atom to isolate the atomic or group contributions to measurable molecular properties.

Discussion

The correlation of the delocalization indices for hydrogen atoms with their proton spin−spin coupling constants is an example of how the Fermi exchange density provides the vehicle for the transmission of information between the basins of nonbonded atoms. The transmitted effects have important consequences for reactivity as well, effects that provide further examples of exchange overriding internuclear separations. For example, there is a significantly greater delocalization of the π density of a carbon atom in benzene onto the para rather than the meta carbon. The same pattern of delocalization is found for the corresponding atoms relative to the carbon bearing an electron-releasing substituent such as NH_2 and for the same atoms relative to the nitrogen atom in pyridine. Thus the delocalization pattern of the Fermi correlation parallels the reactivity patterns of substituted benzene and related aromatic molecules.[7,8]

The same pattern of alternating behavior is displayed by the Laplacian of the electron density in substituted benzenes for which the greatest charge concentrations defined by its topology are located para to the carbon bearing an electron-releasing substituent and meta to that bearing an electron-withdrawing one.[24] This association is not unexpected because the topology of the Laplacian of the electron density provides a mapping of the essential pairing information from six- to three-dimensional space, as determined by the properties of the Fermi density. This statement follows from the form of the conditional same-spin pair density, $[\rho^{\alpha}(\mathbf{r}_2) + h^{\alpha}(\mathbf{r}_1,\mathbf{r}_2)]$: when the density of the Fermi hole is localized in the vicinity of $\mathbf{r}_1$, then the conditional pair density reduces to the spin density at points $\mathbf{r}_2$ removed from $\mathbf{r}_1$. Under these conditions, the Laplacian of the conditional pair density for a closed-shell system, the concentrations of which indicate where the density of the remaining electron pairs is to be found for a fixed position of a reference pair, will reduce to the Laplacian of the total density. Indeed, the two fields have been demonstrated to be structurally homeomorphic.[25] Thus the local maxima in the field $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$, the local charge concentrations (CCs) of the Laplacian, denote regions of partial pair condensation, regions with greater than average probability of occupation by a single pair of electrons. The number, relative size, and orientation of the CCs of $L(\mathbf{r})$ provide a remarkably faithful mapping of the localized bonded and nonbonded Lewis pairs assumed in the VSEPR model of molecular geometry.[26]

The CCs of the Laplacian denote regions of localization of the Fermi correlation, concentrations that correlate with the localization index, $\lambda(\mathrm{A})$. Just as the total Fermi correlation sums to $-N$, it sums separately to $-N(\mathrm{A})$, the population of each atom. Thus, one has $N^{\alpha}(\mathrm{A}) = \lambda^{\alpha}(\mathrm{A}) + \sum_{\mathrm{B}\neq\mathrm{A}}\delta^{\alpha}(\mathrm{A,B})/2$, an expression detailing how the population of atom A that is not localized on A is spread out into the basins of each of the remaining atoms in the molecule. Thus, both the localization of electrons determined by the CCs of $L(\mathbf{r})$ and their delocalization determined by the index $\delta(\mathrm{A,B})$ are manifestations of the density of the Fermi hole and are grounded in the physics of the pair density.

Wilkens et al.[16] have used the natural bond orbital (NBO) approach to calculate and analyze the Fermi contact contributions to $J_{\mathrm{HH}'}$, while Esteban et al.[27] use the same approach to investigate the bond−antibond interactions in an analysis of vicinal proton−proton coupling constants. The results obtained in these studies are dependent upon the use of the specific choice of NBOs and natural localized molecular orbitals, chosen to be in close correspondence with the Lewis structure representation. Esteban et al. note that this choice of orbital representation yields an interpretation different from the one obtained in an approach labeled IPPP-CLOPA that employs a different set of localized molecular orbitals. [27]

The present paper differs from these in that its purpose is not to interpret a calculated coupling constant but rather to demonstrate that the Fermi contact term can be successfully *modeled* in terms of the exchange density and thus by the delocalization of the electrons between the basins of the associated hydrogen atoms. Whatever the application, QTAIM and a NBO analysis do represent different philosophies. Unlike the NBO approach, the exchange density and the electron delocalization that it determines are invariant to the choice of orbitals used in their representation. What set of orbitals is used to determine the delocalization of electrons between two atomic basins is unimportant compared to the ability to uniquely define the extent of delocalization and determine its physical consequences. In addition, the Lewis model is not built into the physics of an open system. Instead, its many facets are recovered in the properties of the pair density: in the bond orders determined by the delocalization index and in the spatial structuring of the bonded and nonbonded Lewis pairs revealed in the topology displayed by the CCs of the Laplacian of the electron density, as determined by the conditional pair density.

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