

coefficient, which for both sets of data was 0.95. However, the theoretical slope of $K = 506$ G was much closer approached by the annihilated spin densities.²⁶ Furthermore, the relative coupling constants for the various hydrogen atoms within any specific radical (e.g., the assignments of the EPR spectra) are much better reproduced by the annihilated correlation.

The drastic changes of spin densities with geometry is very nicely demonstrated by the phenoxy radical, where the "assumed" geometry yields the wrong ordering, while the optimized structure correctly predicts a_H (ortho) $<$ a_H (para).

The strong influence of solvent upon hyperfine interaction is well known and has been tackled by various theoretical models.²⁷ For uncharged, unpolar species as those given in Table III this effect can safely be considered to be negligible.

Conclusions

The reasonable accuracy with which energies, geometries, and spin distributions of radicals are calculated by the unrestricted MINDO/3 open-shell method shows that this treatment is suitable as a predictive tool in radical chemistry. Although for the reason outlined above the radicals are consistently predicted too stable, this method is superior to the half-electron method mainly because of geometry optimization reasons.

Computer Programs. A deck of the MINDO/3-UHF (Unrestricted Hartree Fock) program, including geometry optimization and spin projection, will be deposited with the Quantum Chemistry Program Exchange.

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Extent of Localization of Orbitals in Loges and the Electron Pair Concept

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Abstract: The extent of pair localization in a molecule is discussed in terms of orbitals. It is argued that orbitals may be localized in loges to a degree which is more compatible with the electron pair concept than is suggested by the values of $|F(\Omega, \Omega)/\bar{N}(\Omega)|$, where $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ is the fractional localization of electrons in loge Ω , $\bar{N}(\Omega)$ is the average number of electrons in Ω , and $F(\Omega, \Omega)$ is equal to the fluctuation in the population of Ω minus $\bar{N}(\Omega)$. Consider an N -electron closed shell system described by a Hartree-Fock wave function consisting of $N/2$ space orbitals. Let μ_1 be that orbital in the Hartree-Fock space which has the largest fraction of its charge density within the loge Ω . This fraction is equal to $\langle \mu_1 | \mu_1 \rangle_{\Omega}$, where $\langle \mu_1 | \mu_1 \rangle_{\Omega}$ is the overlap of μ_1 with itself over the region Ω . In addition, if $\bar{N}(\Omega) = 2$, then $\langle \mu_1 | \mu_1 \rangle_{\Omega}$ also turns out to be the fractional contribution of μ_1 to the average number of electrons in Ω . Thus $\langle \mu_1 | \mu_1 \rangle_{\Omega}$ should serve as a reasonable assessment of the extent of localization of μ_1 within Ω . The value of $\langle \mu_1 | \mu_1 \rangle_{\Omega}$ may be significantly larger than the value of $|F(\Omega, \Omega)/\bar{N}(\Omega)|$. For example, in the CH bond loge of CH₄, $\langle \mu_1 | \mu_1 \rangle_{\Omega} = 0.82$ while $|F(\Omega, \Omega)/\bar{N}(\Omega)| = 0.69$. Furthermore, it is shown that $\langle \mu_1 | \mu_1 \rangle_{\Omega}$ is often approximately equal to $|F(\Omega, \Omega)/\bar{N}(\Omega)|^{1/2}$.

Introduction

The electron pair concept has been a central feature of chemistry. It is therefore pertinent that the recent important work of Bader and Stephens^{1a} implies that the model of spatially localized pairs is not quite suitable for many molecules.

For instance, the model was argued to be of only borderline applicability in CH₄. With this in mind, it is the purpose of this article to discuss the question of pair localization in terms of the maximum extent that an orbital may be localized within a loge.²

Table I. Extent of Core Localizations^a

Molecule	$\bar{N}(\Omega)$	$ F(\Omega, \Omega)/\bar{N}(\Omega) $	$ F(\Omega, \Omega)/\bar{N}(\Omega) ^{1/2}$	$\langle \mu_1 \mu_1 \rangle_\Omega$
LiH	1.999	0.96	0.98	0.98
BH	2.002	0.92	0.96	
BeH ₂	2.012	0.93	0.96	0.97
BH ₃	2.023	0.91	0.95	0.96
BH ₄ ⁻	2.026	0.90	0.95	0.95
CH ₄	2.005	0.88	0.94	0.94
NH ₃	2.002	0.86	0.93	
H ₂ O	2.001	0.84	0.92	
HF	1.966	0.82	0.91	
N ₂	2.001	0.87	0.93	
F ₂	2.008	0.83	0.91	
Ne	1.963	0.77	0.88	0.87
Ar	1.856	0.73	0.85	

^a Where there was sufficient symmetry, $\langle \mu_1 | \mu_1 \rangle_\Omega$ was computed from the data given in Table I of ref 1a or Table I of ref 1b.

Table II. Extent of Bond Localizations^a

Molecule	$\bar{N}(\Omega)$	$ F(\Omega, \Omega)/\bar{N}(\Omega) $	$ F(\Omega, \Omega)/\bar{N}(\Omega) ^{1/2}$	$\langle \mu_1 \mu_1 \rangle_\Omega$
LiH	2.001	0.96	0.98	0.98
BH	2.000	0.87	0.93	0.93
BeH ₂	1.994	0.93	0.96	0.96
BH ₃	1.992	0.82	0.90	0.90
BH ₄ ⁻	1.994	0.76	0.87	0.87
CH ₄	1.999	0.69	0.83	0.82
NH ₃	1.997	0.68	0.82	
H ₂ O	1.987	0.56	0.75	
HF	2.037	0.53	0.73	0.71
N ₂ (σ)	1.995	0.28	0.53	
N ₂ (π)	1.966	0.29	0.54	
F ₂	2.034	0.17	0.42	0.30

^a Where there was sufficient symmetry, $\langle \mu_1 | \mu_1 \rangle_\Omega$ was computed from the data given in Table II of ref 1a or Table I of ref 1b. In addition, it was assumed that $|F(\Omega, \Omega)/\bar{N}(\Omega)| = 1$ for the core loges. This assumption should have little, if any, effect upon the reported values of $\langle \mu_1 | \mu_1 \rangle_\Omega$.

One of the major localization criteria used by Bader and Stephens¹ was $|F(\Omega, \Omega)/\bar{N}(\Omega)| \times 100$. This was employed by the authors to signify the percentage localization of the electrons in region Ω , where

$$F(\Omega, \Omega) = \Lambda(\Omega) - \bar{N}(\Omega) \quad (1)$$

$\bar{N}(\Omega)$ is the average number of electrons in loge Ω and $\Lambda(\Omega)$ is the fluctuation in the population of Ω . For a system of N electrons, the fluctuation is defined by

$$\Lambda(\Omega) = \sum_{n=0}^N P_n(\Omega)(n - \bar{N}(\Omega))^2 \quad (2)$$

where $P_n(\Omega)$ is the probability of the event that n electrons will be found in Ω when the other $N - n$ electrons are confined to the remaining space. Since $\Lambda(\Omega) \geq 0$, it follows from eq 1 that

$$-F(\Omega, \Omega)/\bar{N}(\Omega) \leq 1 \quad (3)$$

In addition, $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ would equal unity only if the probability were unity for the event that $\bar{N}(\Omega)$ electrons will be found in Ω when the other $N - \bar{N}(\Omega)$ electrons are confined to the remaining space. Furthermore, Bader and Stephens show¹ that $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ is the fraction of the total possible correlation per electron contained in Ω . Thus, $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ is meaningful as a measure of the extent of localization of electrons in Ω . The best decomposition into $N/2$ loges is obtained by simultaneously maximizing $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ for each

Table III. Extent of Nonbonded Localizations^a

Molecule	$\bar{N}(\Omega)$	$ F(\Omega, \Omega)/\bar{N}(\Omega) $	$ F(\Omega, \Omega)/\bar{N}(\Omega) ^{1/2}$	$\langle \mu_1 \mu_1 \rangle_\Omega$
BH	1.998	0.85	0.92	0.92
NH ₃	2.005	0.55	0.74	0.73
H ₂ O	2.005	0.52	0.72	
HF	1.999	0.49	0.70	
Ne	2.009	0.48	0.69	0.67
N ₂	2.035	0.59	0.77	

^a Where there was sufficient symmetry, $\langle \mu_1 | \mu_1 \rangle_\Omega$ was computed from the data given in Table III of ref 1a and Table I of ref 1b. In addition, it was assumed that $|F(\Omega, \Omega)/\bar{N}(\Omega)| = 1$ for core loges. This assumption should have little, if any, effect upon the reported values of $\langle \mu_1 | \mu_1 \rangle_\Omega$.

region. This is equivalent to minimizing the sum of the fluctuations in the loge populations.

What is significant is the fact that in situations where one has traditionally believed the pair concept to be intact, the fractional localization, defined as $|F(\Omega, \Omega)/\bar{N}(\Omega)|$, often turns out to be much lower than expected. Witness the core loge of Ne where the degree of localization, as listed in Table I, is reported by Bader and Stephens^{1a} to be only 77%, or the bond loges of CH₄ and H₂O, where the extents of localization, as listed in Table II, are reported to be only 69 and 56%, respectively.^{1a}

Recent studies indicate that geminals and localized Hartree-Fock orbitals are generally transferable.^{3,4} These studies support the pair concept. It is thus natural to attempt to find the connection between localized orbitals and loges and to investigate the possible extent of localization of orbitals in the loges. We shall show that orbitals can be localized in the loges to a greater degree than suggested by the values of $|F(\Omega, \Omega)/\bar{N}(\Omega)|$.

Theory

Let us consider a closed shell system of N electrons composed of the $N/2$ orthonormal space orbitals $\{\lambda_i\}$ which constitute the Hartree-Fock wave function. In terms of these orbitals,¹

$$F(\Omega, \Omega) = -2 \sum_{i,j}^{N/2} S_{ij}^2(\Omega) \quad (4)$$

where $S_{ij}(\Omega) \equiv \langle \lambda_i | \lambda_j \rangle_\Omega$. The matrix element $\langle \lambda_i | \lambda_j \rangle_\Omega$ is the overlap of the orbitals λ_i and λ_j in the region Ω . Now, by diagonalizing $\mathbf{S}(\Omega)$, we form the new set of orbitals $\{\mu_i\}$ from $\{\lambda_i\}$ such that $\langle \mu_i | \mu_j \rangle_\Omega = \delta_{ij} \langle \mu_i | \mu_i \rangle_\Omega$. In terms of $\{\mu_i\}$, $F(\Omega, \Omega)$ and $\bar{N}(\Omega)$ are given by

$$F(\Omega, \Omega) = -2 \sum_i^{N/2} \langle \mu_i | \mu_i \rangle_\Omega^2 \quad (5)$$

$$\bar{N}(\Omega) = 2 \sum_i \langle \mu_i | \mu_i \rangle_\Omega \quad (6)$$

Let $\langle \mu_1 | \mu_1 \rangle_\Omega$ denote the highest eigenvalue of $\mathbf{S}(\Omega)$. The orbital μ_1 is then simply that function in the Hartree-Fock space which has the largest fraction of its charge density within Ω .⁵ This fraction is equal to $\langle \mu_1 | \mu_1 \rangle_\Omega$. Furthermore, if $\bar{N}(\Omega) = 2$, which is essentially the case for most loges reported by Bader and Stephens,¹ then $\langle \mu_1 | \mu_1 \rangle_\Omega = 2 \langle \mu_1 | \mu_1 \rangle_\Omega / \bar{N}(\Omega)$, so that $\langle \mu_1 | \mu_1 \rangle_\Omega$ also turns out to be the fractional contribution of μ_1 to $\bar{N}(\Omega)$. Thus $\langle \mu_1 | \mu_1 \rangle_\Omega$ should generally provide a very reasonable assessment of the extent of localization of μ_1 within Ω . Perfect pair separability requires that $\langle \mu_1 | \mu_1 \rangle_\Omega = 1$.

Results and Discussion

Values for $\langle \mu_1 | \mu_1 \rangle_\Omega$ are reported in Tables I-III. Note that in all cases $\langle \mu_1 | \mu_1 \rangle_\Omega$ is larger than $|F(\Omega, \Omega)/\bar{N}(\Omega)|$, indicating

that the orbitals are more localized than suggested by the values of $|F(\Omega, \Omega)/\bar{N}(\Omega)|$. For instance, the value for $\langle \mu_1 | \mu_1 \rangle_\Omega \times 100$ in the CH bond lobe is 82%. This figure is definitely more compatible with the electron pair concept than is the figure of 69% which is obtained from $|F(\Omega, \Omega)/\bar{N}(\Omega)|$. It should be noted, however, that the value of $\langle \mu_1 | \mu_1 \rangle_\Omega$ in the F₂ bond lobe is as low as 0.30. It is also important to note that Bader and Stephens found^{1a} that no single region of the space of the valence density of CH₄, NH₃, H₂O, or Ne exhibits a minimum in its fluctuation.⁶

For a closed shell system, the relationship between $\langle \mu_1 | \mu_1 \rangle_\Omega$ and $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ is

$$\langle \mu_1 | \mu_1 \rangle_\Omega^2 = \frac{\bar{N}(\Omega)}{2} |F(\Omega, \Omega)/\bar{N}(\Omega)| - \sum_{i \neq 1} \langle \mu_i | \mu_i \rangle_\Omega^2 \quad (7)$$

From the above relationship, if $\bar{N}(\Omega) \leq 2$, then $\langle \mu_1 | \mu_1 \rangle_\Omega < |F(\Omega, \Omega)/\bar{N}(\Omega)|^{1/2}$. However, if $\bar{N}(\Omega)$ is close to 2, which is usually the case, and if $|F(\Omega, \Omega)/\bar{N}(\Omega)|$ is not extremely small, then the following simple approximate relationship must hold because $\langle \mu_1 | \mu_1 \rangle_\Omega^2 \gg \langle \mu_i | \mu_i \rangle_\Omega^2$ ($i \neq 1$):

$$\langle \mu_1 | \mu_1 \rangle_\Omega \approx |F(\Omega, \Omega)/\bar{N}(\Omega)|^{1/2} \quad (8)$$

Tables I-III confirm the validity of eq 8. Consequently, for many lobes, $\langle \mu_1 | \mu_1 \rangle_\Omega$ should yield a significantly higher number than $|F(\Omega, \Omega)/\bar{N}(\Omega)|$; witness $|F(\Omega, \Omega)/\bar{N}(\Omega)|^{1/2}$ for

the bond lobes of BH₄⁻, NH₃, and H₂O.

In conclusion, we have emphasized that it is worthwhile to investigate the extent of pair localization in a molecule in terms of orbitals as well as in terms of the localizability of the Fermi hole.

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- (6) Descriptions of valence lobes for these systems are given on p 17 and 18 of ref 1a.

Correlation Effects on Barriers to Proton Transfer in Intramolecular Hydrogen Bonds. The Enol Tautomer of Malondialdehyde Studied by ab Initio SCF-CI Calculations

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Abstract: Ab initio MO-LCAO-SCF-CI calculations have been performed on the enol tautomer of malondialdehyde, the parent compound for β -dicarbonyls. The molecule contains an intramolecular hydrogen bond, the potential of which is found to be of the double-well type. Previous calculations of the barrier height performed on the SCF level yielded a value of 48 kJ/mol. The present study includes correlation effects which reduce the barrier height to 42 kJ/mol.

The enol tautomers of β -dicarbonyl compounds are usually stabilized by a strong intramolecular hydrogen bond. A much debated question has been if this hydrogen bond is strong enough to result in a single minimum potential for the proton or if it is of the double minimum type. The two possibilities are illustrated in Figure 1 for the parent β -dicarbonyl compound malondialdehyde (MA). In order to study the problem regarding the shape of the hydrogen bond potential we recently performed a series of ab initio MO-LCAO-SCF calculations of MA.² The results from this study clearly indicated that this compound has a C_s symmetric structure with a double minimum potential. Independently Isacson and Morokuma³ have reached the opposite conclusion, that the C_{2v} form is the most stable, also from an MO-LCAO-SCF calculation. The source of this discrepancy is probably that Isacson and Morokuma only performed a very restricted geometry optimization of the C_s form which prevented them from finding the C_s minimum structure.

There exists as yet very little experimental data on the structure of MA, but the analogous compound 2,4-pentanedione (acetylacetone) has been extensively studied. The results of different techniques are however incompatible. In two studies using electron diffraction^{4,5} acetylacetone was found to have C_{2v} symmetry while both ir⁶ and NMR⁷ studies have shown acetylacetone to have an asymmetric hydrogen bond.

In our previous SCF study of MA² it was concluded that the most serious error in the calculation might be due to the neglect of correlation effects. Studies of smaller systems such as H₃O₂⁻, HF₂⁻, and H₅O₂⁺ have shown that correlation effects can be of considerable importance for the shape and barrier height of hydrogen bond potentials.^{8,9} Very accurate CI calculations on H₃O₂⁻ using an extended basis set and accounting for 75% of the total valence shell correlation energy^{8b} actually yielded a proton transfer barrier of only 0.6 kJ/mol while the corresponding value obtained on the SCF level of approximation was 6.0 kJ/mol. Very similar results were obtained in