

ON THE NATURE OF LOCALIZED ORBITALS IN SOME σ - AND π -ELECTRON SYSTEMS

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Localization of various types of σ - and π - bond orbitals in nonaromatic and aromatic systems is discussed on the basis of numerical results. A comparison of the electronic structures of the molecules C_2H_2 , C_2H_4 , HCN, and H_2O , as described by the INDO SCF canonical molecular orbitals and by strictly localized orbitals, is given in terms of electron density maps.

Localized orbitals (LO's) have been proved to be useful for chemical interpretation of electron wave functions and approximate description of molecular electronic structure. Several localization procedures¹ for finding localized functions, have been developed differing in the localization criteria and in the possibilities of application. Among those the method based on the construction of "localized natural" orbitals²⁻⁴ is one of the simplest as it relies only upon the projection property of the Fock-Dirac density matrix ρ . Recently, Robj⁵ reported an approach which is quite close to that one just mentioned. The method of localized natural orbitals was applied to various kinds of problems⁶⁻⁹. A particular attention was paid to studying the extents of localizability and transferability of lone pair and bond orbitals⁶⁻⁸, to examining the possibility of constructing minimum contracted basis sets by means of LO's⁹, and to the problem of using LO's as the zero approximation in a SC perturbation treatment¹⁰. In our former studies it appeared to be sometimes convenient to perform computations on molecules within semiempirical schemes. Of course, it is true that semiempirical methods are less satisfying intellectually, although they frequently have the advantage of greater tractability. However, it is commonly believed that especially the INDO method¹¹ takes a reasonable account of the localized electron properties and charge density distributions¹²⁻¹⁴, while still being easily applicable to large molecules. For these reasons the work reported in this paper mostly employs the INDO Hamiltonian.

The present study has been undertaken with a twofold objective: on the one hand, to examine the limits of localizability of various kinds of bond orbitals; on the other hand, to explore and to visualize the difference between the SCF molecular orbital and approximative (strictly localized) orbital descriptions of some representative electronic systems.

THEORETICAL

The strictly localized orbital (SLO) describing the electron pair of the bond between the atoms A and B can be expressed as

$$\eta_{AB} = q(\varphi_A + b\varphi_B), \quad (1)$$

where φ'_i , b and q denote the hybrid orbitals (HO's), the bond polarity parameter and the normalization constant, respectively. On using the criterion of maximum

TABLE I
Characteristics of Optimum σ Bond Orbitals (analysis of INDO type calculations)

Molecule	Bond A—B	s-Character		n
		A	B	
C ₂ H ₂	C1—C2	55.1	55.1	1.992
C ₂ H ₄	C1—C2	38.9	38.9	1.999
C ₃ H ₆ , stagg ^a	C1—C2	29.0	33.5	1.984
	C2—C3	39.4	40.0	1.992
C ₄ H ₆ , trans ^b	C1—C2	39.5	38.3	1.994
	C2—C3	33.3	33.3	1.968
C ₂ H ₆	C1—C2	27.6	27.6	2.000
HCN	C—N	53.4	30.5	1.993
	C—H	46.6	—	1.992
NH ₃	N—H	20.9	—	1.999
H ₂ O	O—H	17.0	—	2.000
H ₂ CO	C—O	32.3	26.8	1.998
	C—H	33.9	—	1.992

^a Structure I. ^b Structure II.

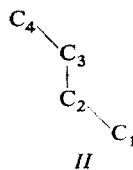
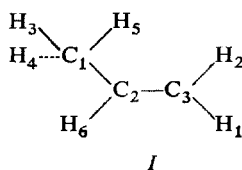


TABLE II
Characteristics of Localized π Orbitals for *trans* Butadiene and Benzene (analysis of INDO type calculations)

Molecule	C ₄ H ₆				C ₆ H ₆
	Bond	C1—C2	C2—C3	C1—C3	C1—C4
n	1.957	1.275	1.014	1.303	1.667

projection of the localized function onto the Hartree–Fock manifold

$$n = \max [\eta_{AB}^+ \rho \eta_{AB}], \quad (2)$$

where ρ is the spinless Hartree–Fock density matrix, either optimum hybrids^{3,4} or optimum bond orbitals⁴ at given hybrids can be calculated. It should be stressed that the number n can be considered as the quantitative measure of localizability and that it can reach the value 2 in the case, when the given localized orbital is fully occupied by two electrons.

In our former studies we employed two means for the appraisal of the degree of coincidence between the SCF solution of the problem and the strictly localized orbital picture of the electronic system under study. Namely, the difference in mean values of energies and the overlap integral, both corresponding to the “accurate” (*i.e.* SCF) and approximate single determinant wave functions. It seemed, therefore, interesting to complement the original assessment by adding some information on the comparison of the overall behaviour of both types of wave functions. This can be suitably done by determining the difference in electron density distributions between the two wave functions of the same molecule. Since the basis set in the INDO framework consists of effectively orthogonal atomic orbitals, we accepted the assumption that between them and the Slater-type orbitals χ_S exists a relationship which can be expressed by means of the Löwdin symmetric transformation^{15,16}. Hence the electron density function $P(r)$ for a closed shell system can be written as

$$P(r) = 2\chi_S(r) C'(C')^+ \chi_S^+(r), \quad (3)$$

$$C' = S^{-1/2} C, \quad (4)$$

TABLE III

Benzene Molecule. Molecular Energies (a.u.) and Gross Charges on the Carbon Atom (a.u.) Obtained by Various SC-Perturbation Treatments Based on the INDO Type Parametrization

Perturbation energies are given relative to the SCF value -45.57554 a.u. (Carbon gross charge SCF value: 0.0245 a.u.)

Zero-order functions	Perturbation solution	Molecular energy	Carbon gross charge
σ SLO's, π SLO's	0. order	0.57220	0
	I. order decoupled	0.09670	0.0116
	I. order coupled	0.01042	0.0277
σ SLO's, π SCF	0. order	0.24378	0
	I. order decoupled	0.01382	0.0116
	I. order coupled	0.00009	0.0277

where \mathbf{C} is the LCAO MO coefficient matrix of occupied orbitals related to the orthogonal AO basis set and \mathbf{S} is the overlap matrix corresponding to Slater-type atomic orbitals. The exponents were chosen according to the Slater rules with the exception of the 1s hydrogen orbital, for which the value 1.2 was taken¹⁷. The relevant difference function is defined as

$$\Delta P(r) = P_{\text{SLO}}(r) - P_{\text{SCF}}(r), \quad (5)$$

where the symbols P_{SLO} a P_{SCF} denote density functions obtained from the SLO and SCF MO electron descriptions, respectively.

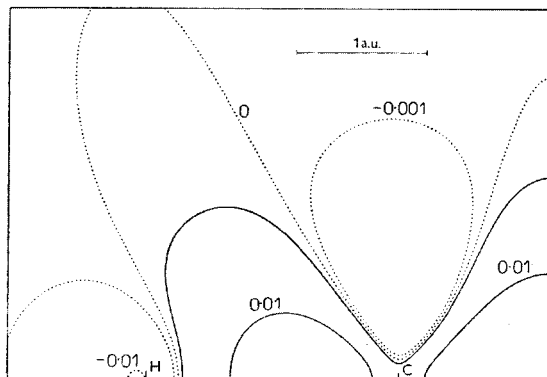


FIG. 1

Acetylene. Difference Density in the Plane Containing the Molecular Axis. All the Difference Density Maps are in Atomic Units

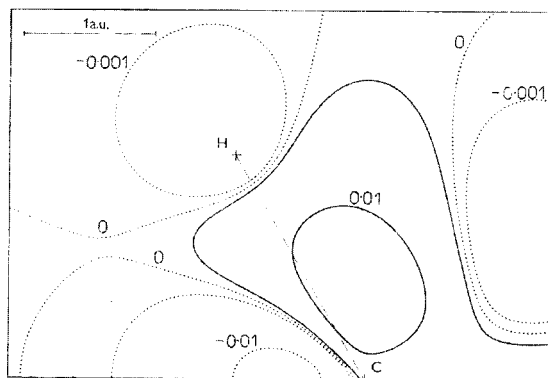


FIG. 2

Ethylene. Difference Density in the Plane of the Molecule

RESULTS AND DISCUSSION

The localization approach mentioned in the previous section has been applied to the INDO SCF wave functions of a number of hydrocarbons and to molecules H_2O , HCN , NH_3 and H_2CO . Their equilibrium geometries were taken the same as in the papers^{3,10}. For the benzene molecule we have used the data $d(\text{C}-\text{C}) = 1.395 \text{ \AA}$ and $d(\text{C}-\text{H}) = 1.085 \text{ \AA}$.

Table I presents important parameters characterizing the optimum SLO's constructed by means of optimum hybrids for some types of σ bonds. As it is seen from this table and from Table I of paper⁸, the values of the occupation number n range from 1.98 to 2.00 in almost all cases, except the C2-C3 and C2-H3 bonds in butadiene (*trans* and *cis*), and C3-H6 bond in propylene (staggered and eclipsed). The same values of n are typical for lone pair orbitals⁷.

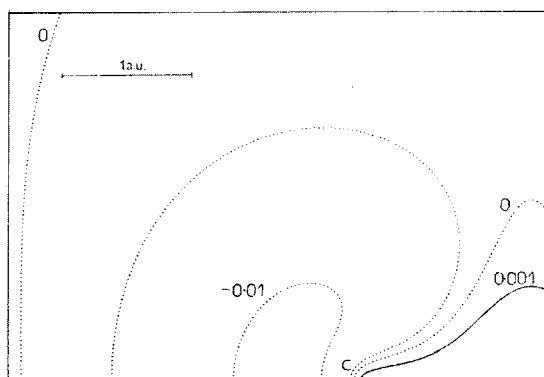


FIG. 3
Ethylene. Difference Density in the Plane Containing the C—C Bond, Perpendicular to the Molecular Plane

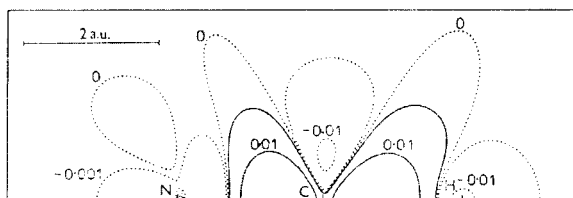


FIG. 4
Hydrogen Cyanide. Difference Density in the Plane Containing the Molecular Axis

As regards the orbitals of π symmetry, however, there would seem to be a fundamental difference in localizability compared to σ orbitals. Surprisingly enough, it was found by Diner and collaborators¹⁸ that the extent of localization in some π - and σ -electron systems is well comparable. We came to the same conclusion on grounds of analyzing π orbitals of both isomers of butadiene⁸. Therefore, it seemed interesting to explore and to demonstrate the delocalization with π systems of aromatic hydrocarbons. In previous studies the localization procedure defined by minimizing molecular exchange energy¹⁹ has been applied to π orbitals of aromatic and nonaromatic hydrocarbons²⁰⁻²² in order to obtain information on various types of

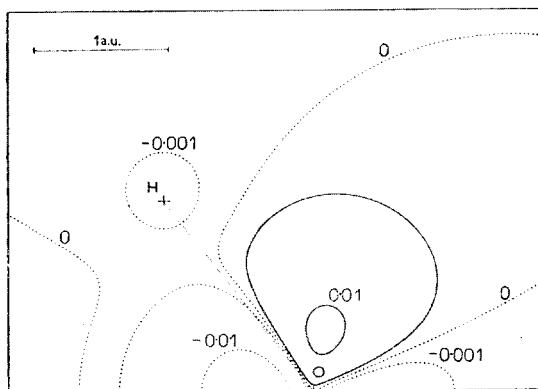


FIG. 5
Water. Difference Density in the Plane of the Molecule

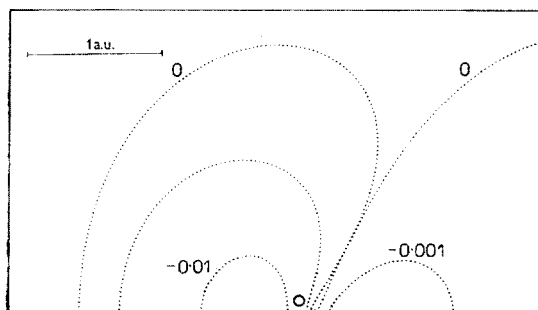


FIG. 6
Water. Difference Density in the Plane Bisecting the HOH Angle, Perpendicular to the Molecular Plane

classical and nonclassical bonding. In contrast to this approach, the localization procedure mentioned above is capable of yielding the direct measure of localization in the form of the quantity n . To help evaluate the significance of the value n for the localized π bond of benzene, we have it combined in Table II with occupation numbers previously obtained⁸ for various hypothetical two-centre π bonds in butadiene. Clearly the localization in benzene is much less than that corresponding to the π bond C1–C2 (and C3–C4) in butadiene. Of course, this result for an aromatic system is interesting but not surprising, since it is in accordance with the chemical feeling.

The nature of π -electron delocalization also manifests itself in the SC-perturbation treatment¹⁰ of the benzene molecule. As the starting point for the calculations we used the transferable SLO's suggested for the C–H and C–C bonds in paper¹⁰, ("directed" HO's; $b = 1.00$), and the π orbitals taken either from the SCF calculation or approximated as bond orbitals with $b = 1.0$, located at neighbouring sites, as in the classical hypothesis of Kekulé. The results are summarized in Table III, which presents, for each case, molecular energies and atomic gross charges corresponding to various types of approximation. The details of these calculations have been reported elsewhere¹⁰. As anticipated, the use of π SLO's exerts a salient influence on the calculated values. Whereas in the case of butadiene, within the same level of approximation the perturbation calculation yields energies and charges close to the SCF values (Table II of paper¹⁰), with benzene the SLO description of π orbitals leads to a considerable deterioration of the results compared to those which are related to the SCF π -molecular orbitals.

A final point of interest will be the examination of SLO's by means of the valence electron density functions, as defined by Eq. (5). The density difference functions were calculated and plotted for four illustrative examples, namely for the molecules C_2H_2 , C_2H_4 , HCN and H_2O . The SLO description of these molecules is based on optimum SLO's built up of optimum hybrids^{3,4}. The levels of all the density difference maps are drawn at the values ± 0.001 , ± 0.01 and 0 a.u., the dashed and solid contours correspond to the non-positive (*i.e.* negative and zero) and positive values, respectively. The use of atomic units means that the charge density is given in proton charge per (a.u.)³. Atomic locations and line segments indicate the scale of the figures.

In Figs 1,2 and 3 the function $\Delta P(r)$ is plotted for the hydrocarbons. As expected, an increase of charge has occurred in the internuclear regions, accompanied by a decrease in charge density to the outsides of the bonding regions. We observe that the hydrogen nucleus lies within the negative part of the diagram. The density difference function for HCN is plotted in Fig. 4. It has the same general features as have previously been observed in the density difference functions of the unpolar molecules. It is noticeable, however, that the SLO lone pair description is quite satisfactory. A remarkable situation is encountered with H_2O , as can be seen from the level diagrams of the density difference in Figs 5 and 6. We have density difference maxima symmetrically arranged about the molecular symmetry axis, outside of the triangle

formed by the oxygen and two hydrogen atoms. This phenomenon indicates that the SLO description overestimates the valence angle of the bent bond structure of the water molecule. Thus, we can conclude that the exaggeration of electronic charge either in straight or bent bonds is a typical feature of the SLO description.

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