ON THE TRANSFERABILITY OF BOND ORBITALS
IN HYDROCARBONS

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This paper presents the results of applications of the localization method developed previously to various types of wave functions in the hydrocarbon series. The localization criterion of this method is based on the maximum projection of bond orbitals onto the space spanned by occupied SCF orbitals. Localizability and transferability of sigma and pi orbitals are discussed on the basis of numerical results. The system of strictly localized orbitals has been examined from the viewpoint of its use as a zero approximation for calculations of higher accuracy.

At the time of modern chemistry, it has been found convenient to predict and interpret properties of molecular electronic systems by means of properties of localized electrons, as *e.g.* inner shells electrons, lone electron pairs, and electrons in localized bonds. This fact stimulated attempts to develop methods[1] which would permit to analyze complex wave functions in terms of these concepts. The form of the functions describing groups of localized electrons and the method of their construction are dependent upon the level of approximation adopted in actual calculations. In the case with the single-determinant ground state wave function for a closed shell electronic system, the task of finding localized functions is compatible with the problem of finding one-electron localized functions, *i.e.* localized orbitals (LO's). Within the framework of the one-particle approximation, each physical situation can completely be described by the first order density matrix[2]. The invariance of the first order density matrix with respect to unitary transformations permits to construct LO's according to certain criteria. The LO's are thus equivalent to canonical molecular orbitals (MO's) (the latter being solutions of the standard Hartree–Fock problem) inasmuch as the mean values of physical quantities remain unaffected. The LO's are not solely localized in certain parts of molecules, but exhibit a non-vanishing electron density along the entire molecule. Accordingly, one cannot separate electron pairs so that each of them would expand over the region defined only by one or two centers. The method developed recently[3-5] permits to derive a single-determinant wave function in such a way that the resulting optimum localized orbitals (SLO's) are located on a given number of centers. Although the N-electron function constructed from the SLO's is lacking the property of being optimized with respect to the variational principle, the SLO's for a given type of bond can be anticipated to be transferable from molecule to molecule. Experimental results on Compton X-ray diffraction[6,7] established the localizability and transferability of bonds in hydrocarbons and provided the justification for theoretical analyses of wave functions along these lines[8-10].

This paper summarizes the results of applications of the localization procedure just mentioned[3,4] to various types of wave functions in the series of hydrocarbons.

In discussion, the following aspects are emphasized: the extents of localizability and transferability of σ- and π-orbitals; the possibility to estimate the degree of coincidence between the SCF solution and its approximation based on SLO's by means of the overlap integral between the normalized Slater determinants corresponding to both kinds of orbital description; and the use of the SLO's as a zero approximation for calculations of higher accuracy.

THEORETICAL

The optimum SLO's are defined so as to fulfil the requirement of the maximum projection onto the space spanned by occupied SCF molecular orbitals[3,4]

$$n = \max \left[\boldsymbol{\eta}^+ \varrho \boldsymbol{\eta} \right], \qquad (1)$$

where ϱ is the spinless first order density matrix and n is the "occupation number" of the pertinent localized orbital $\boldsymbol{\eta}$. The SLO $\boldsymbol{\eta}$, describing the electron pair of the AB bond, can be expressed as

$$\boldsymbol{\eta} \equiv \boldsymbol{\eta}_{AB} = q \left(\varphi_A + b\varphi_B \right), \qquad (2)$$

where φ_I means the hybrid orbital (HO) localized on the atom I, the b parameter reflects the polarity of the AB bond, and q is the normalization constant. The crition (1) has been specified for two cases: a) The optimum HO's, φ_I, I = A, B, were determined as linear combinations of atomic orbitals on atoms A and B[4,5]. b) The optimum b parameter was found for fixed HO's on the two atoms[3]. The optimum HO's localized on one center were constrained to orthonormality.

The method characterizes a localized electron pair by means of two quantities: the localized function $\boldsymbol{\eta}$ and the occupation number n which can be considered as a quantitative measure of localizability. The present method is superior to existing localization procedures[1] because of its simplicity and little computational cost involved in calculations, and because it permits to treat a specific part of molecule without considering the other one explicitly.

RESULTS AND DISCUSSION

The presented method has been applied to wave functions for methane, acetylene, ethane, ethylene, staggered and eclipsed propylenes, *cis* and *trans* butadienes. The EHT (ref.[11]) and CNDO (ref.[12]) type wave functions have been available for all molecules under study, with the first four molecules, it also was possible to analyze the functions given by *ab initio* calculations[13] in the minimal Slater type orbital basis set. The molecular geometries and the corresponding citations are given in the preceding paper[4], as well as the data on SLO's obtained from the EHT and *ab initio* calculations.

Table I

C—H Bond Orbital Characteristics for Hydrocarbons (analysis of the EHT and INDO types of calculations)

Type of hybridi-zation	Molecule	Bond	EHT		INDO		
			s-character	b	s-character	b	n
sp^3	CH_4		25·0	0·8586	25·0	1·0095	1·9987
	C_2H_6		24·7	0·8778	24·1	1·0189	1·9880
	C_3H_6, stagg.[a]	C1—H3	24·4	0·8584	23·0	1·0201	1·9801
		C1—H5	22·9	0·8787	24·9	1·0168	1·9891
	C_3H_6, ecl.[b]	C1—H3	24·4	0·8567	23·5	1·0182	1·9803
		C1—H5	22·8	0·8736	24·0	1·0206	1·9903
sp^2	C_2H_4		27·9	0·8598	30·6	1·0003	1·9823
	C_3H_6, stagg.	C2—H6	26·0	0·8871	27·1	1·0165	1·9713
		C3—H1	26·7	0·8594	30·0	1·0059	1·9848
		C3—H2	26·4	0·8725	30·0	1·0055	1·9828
	C_3H_6, ecl.	C2—H6	26·1	0·8877	27·1	1·0168	1·9717
		C3—H1	26·9	0·8586	30·0	1·0053	1·9846
		C3—H2	26·3	0·8692	30·0	1·0058	1·9826
	C_4H_6, trans[c]	C1—H1	26·9	0·8607	29·7	1·0057	1·9850
		C1—H2	27·2	0·8658	30·8	1·0011	1·9832
		C2—H3	25·9	0·8863	28·3	1·0135	1·9744
	C_4H_6, cis[c]	C1—H1	26·7	0·8610	29·5	1·0065	1·9849
		C1—H6	27·6	0·8676	30·9	·9978	1·9823
		C2—H2	25·9	0·8803	27·8	1·0160	1·9756
sp	C_2H_2		33·8	0·7742	45·0	·9471	1·9919

[a] Structure *I*, [b] structure *II*, [c] structure *III*.

I   *II*   *III*
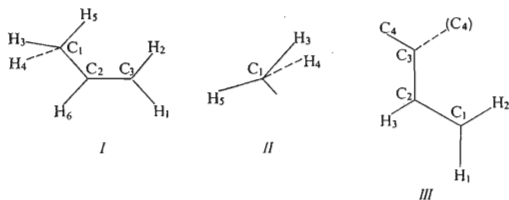
C—H *bond orbitals in hydrocarbons*. The C—H bond has become already the textbook example[14] on the localized electron pair; the characteristic absorption band in infrared spectra (3μ) is even used for both qualitative and quantitative determinations of C—H bonds. This fact stimulated theoretical studies in two directions: either the computational models[15-18] were based on localized C—H bonds assumed *a priori* or the attempts were made to demonstrate a C—H bond orbital as a theoretically identifiable unit by analyzing the wave functions[8-10,19-22].

The parameters characterizing the C—H bond orbitals

$$\eta_{C-H} = q(\varphi_C + b\varphi_H) \tag{3}$$

are listed in Tables I and II. The *s*-character is defined as the percentage contents of the *s* orbital in the HO φ_C centered on the respective carbon. In general, it is possible to state that the type of calculations affects considerably the shapes of C—H bond SLO's but that for a given type of calculations the bond polarity is roughly

TABLE II

C—H Bond Orbital Characteristics for Hydrocarbons (analysis of *ab initio* calculations)

Type of hybridization	Molecule	*s*-Character	*b*
sp^3	CH_4	25·0	0·8531
	C_2H_6	24·4	0·8571
sp^2	C_2H_4	32·5	0·8235
sp	C_2H_2	48·2	0·7117

TABLE III

Characteristics of Localized pi Orbitals for Both Butadiene Isomers (analysis of the INDO type calculations)

Bond[a]	*trans*		*cis*	
	b	*n*	*b*	*n*
C1—C2	0·9857	1·9574	0·9831	1·9590
C2—C3	1·0000	1·2750	1·0000	1·2669
C1—C3	0·1463	1·0144	0·1439	1·0171
C1—C4	−1·0000	1·3026	−1·0000	1·2996

[a] Structure *III*.

dependent on the s-character of the participating carbon HO. Interestingly enough, the SLO's containing sp^3 and sp^2 carbon hybrids are associated with almost the same polarity parameters b, the eventual difference being cancelled by the effect of neighbouring atoms. The deviations from the standard sp^3, sp^2, and sp hybridizations (with the s-characters 25·0, 33·3, and 50·0, respectively) have been discussed in detail previously[4,23,24]. The optimum hybrids given by the INDO Hamiltonian are seen, in Table I, to be close to classical ones. It thus appears possible to replace the optimum hybrids by the directed HO's, the latter being defined for second-row elements in the following way. If k equivalent HO's are to be constructed on a given atom, the HO's of the form $(k)^{-1/2}[(2s) + (k-1)^{1/2}(2p)]$ are set up first. Here $(2p)$ stands for the normalized linear combination of the true spatial $2p$ atomic orbitals. The required orthogonal HO's are obtained by a subsequent symmetry orthogonalization. These HO's do not differ practically from the classical ones and, moreover, can easily be constructed on the basis of the molecular geometry. With so chosen HO's, it is possible to determine the optimum b values, as stated in the point b) of the preceding Section. The values obtained for the C—H bond are again very close to those presented in Table I. It appears that the C—H bond orbitals can be approximated well if b is put equal to 1·02, 1·00, and 0·95 for HO's on sp^3, sp^2, and sp hybridized carbon atoms, respectively.

The transferability of the C—H bond orbital has thoroughly been studied by Rothenberg[8,9] with *ab initio* SCF wave functions for methane, ethane, methanol, ethylene, and acetylene by using the Edmiston–Ruedenberg localization method[25]. The results of that study showed that the effect of extension of the atomic orbital basis set is more important than the effect of substituents and that the C—H bond orbital is transferable well with molecules treated by the same basis set and having the carbon atom of the same type of hybridization. This finding is in accordance with the results of the present paper, attained for semiempirical wave functions.

Localization of π-orbitals. Ordinarily, one differentiates between delocalized pi and localized sigma molecular orbitals. Nevertheless, the application of the localization procedure to pi orbitals also appears to be topical, as it may provide a piece of information on the relation between the MO theory and classical chemical structures[26]. Moreover, it was found by Diner and
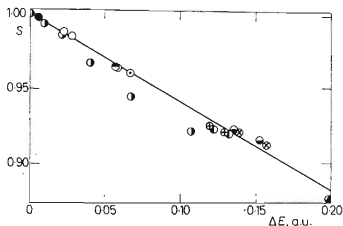

Fig. 1

Plot of the Overlap Integral S against the Difference in Energies Given by SCF and Single-Determinant Functions

● Methane, ○ acetylene, ⊙ ethylene, ◓ ethane, ◐ propylene staggered, ⊕ propylene eclipsed, ⊗ *cis*-butadiene, ◓ *trans*-butadiene, (◑ H_2O, HCN, NH_3, H_2CO)].

collaborators[27] that the characterization of π- and σ-electron orbitals is not justifiable if based on the localization or delocalization properties; for example, the lone electron pairs of the sigma symmetry are more delocalized than the π- electronic systems.

Table III summarizes the results with the INDO type wave functions of *cis* and *trans* butadiene isomers. Here the localization procedure mentioned above was employed with the aim of providing localized orbitals of the π-symmetry. It can be seen that the C1—C2 and C3—C4 bonds are preferred. The occupation number, $n = 1.9574$, is somewhat smaller than those for σ-orbitals (compare Table I), but the differences are not high enough to justify the statement according to which the extent of localization is the principle factor in distinguishing π- and σ-systems. Considerably smaller occupation numbers correspond to C2—C3 and C1—C4 bond orbitals. The lowest occupation number for the C1—C3 bond is in agreement with the Rumer's theorem according to which those VB formulas should be disregarded where a crossing of bonds occurs. With π- systems of aromatic hydrocarbons, of course, it can be anticipated that the delocalization is remarkably superior to that in butadiene.

SLO approximation as zero-order description of molecular systems. The localization procedure used in this paper gives the approximate description of an electronic system in terms of SLO's which are chosen to be in maximal coincidence with the accurate Hartree–Fock solution. The nature of the localization procedure permits to judge this correspondence quantitatively; with respect to the variational nature of the SCF solution, the most appropriate criterion appears to be the difference in mean values of energies corresponding to accurate and approximate single determinant wave functions. This procedure, however, requires computation of molecular integrals. Since the localization procedure alone can avoid computing these integrals, it is convenient to characterize the quality of the SLO approximation by the overlap integral S between the normalized Slater determinants corresponding to accurate and approximate orbital descriptions[4,5,23]. This definition is advantageous particularly in analyzing *ab initio* functions. The restricted number of molecular integrals in the INDO scheme makes it possible to compare directly the two procedures. Fig. 1 presents the plot of overlap integrals S against the respective energy differences within the series of the hydrocarbons studied .With some hydrocarbons several sets of SLO's of differing degrees of optimization were formed. The plot represents a close linear dependence and justifies thus the use of the overlap criterion. It is noteworthy that the data for polar compounds such as H_2O, H_2CO, HCN, and NH_3 also satisfy fairly the linear dependence.

Tables IV and V present the illustration of the effect of the adopted approximations on observables. They comprise total molecular energies (relative to the SCF values), atom charges, and overlap integrals between the SCF and approximate single-determinant functions. With hydrocarbons containing one or two carbon

atoms, the SLO's used were either those obtained by the optimization of HO's and the b parameter (opt. SLO's) or the fixed transferable SLO's (tra. SLO's) The effect of π-orbital localization in butadienes was studied by describing the system either by the SCF MO's (π-SCF) or by localized π-orbitals with $b = 1$. With the approximation using fixed SLO's (tra. SLO's), the C—H bond orbitals were chosen as described in the Section on C—H bonds and the b parameter was put equal to 1 for all C—C bonds. In general it can be stated that the error in predicted total energy is in the worst cases about 10% of the observed heat of atomization (compare[28]). However it should be kept in mind that the INDO approximation with the original parameter set reproduces the heats of atomization even with the 150% error[29]. The charge distribution agrees with that given by the SCF calculation, this agreement being even quantitative for smaller hydrocarbons. With butadienes, the optimalized SLO's give reasonable charge distribution, but the situation becomes less satisfactory on adoption of farther approximations. If the π-system is also described by localized orbitals, the charge distribution becomes uniform all over the molecule.

It is obvious that the description of molecules by means of SLO's is of a limited accuracy. On the other hand, the SLO's appear to be advantageous in those proce-

TABLE IV

Total Molecular Energy, Atomic Charges, and the Overlap Integral S between the SCF and Approximate Single-Determinant Functions for Various Degrees of Approximation of SLO's for CH_4, C_2H_2, C_2H_4, and C_2H_6 Molecules (INDO Hamiltonian)

Molecule	Description	Mol. energy (a.u.)	Gross charges (a.u.)		S
			C	H	
CH_4	SCF	0	0·0378	—0·0095	1·0000
	opt. SLO's	0·00566	0·0379	—0·0095	0·99734
	tra. SLO's	0·00629	0·0792	—0·0198	0·99723
C_2H_2	SCF	0	—0·0537	0·0537	1·0000
	opt. SLO's	0·02267	—0·0543	0·0543	0·98778
	tra. SLO's	0·02879	—0·0512	0·0512	0·98520
C_2H_4	SCF	0	0·0005	—0·0003	1·0000
	opt. SLO's	0·05831	0·0005	—0·0003	0·96441
	tra. SLO's	0·06685	0	0	0·96098
C_2H_6	SCF	0	0·0556	—0·0185	1·0000
	opt. SLO's	0·05664	0·0563	—0·0188	0·96457
	tra. SLO's	0·05920	0·0594	—0·0198	0·96379

TABLE V

Total Molecular Energy, Atomic Charges, and the Overlap Integral S between the SCF and Approximate Single-Determinant Functions for Various Degrees of Approximation of SLO's for Both Butadiene Isomers (INDO Hamiltonian)

Mole-cule	Description	Mol. energy (a.u.)	Gross charges[a] (a.u.)					S
			C1	C2	H1	H2	H3	
trans	SCF	0	−0·0090	0·0328	−0·0085	−0·0023	−0·0130	1·0000
	opt. SLO's, pi SCF	0·13493	−0·0053	0·0255	−0·0057	−0·0011	−0·0134	0·92298
	tra. SLO's, pi SCF	0·15113	−0·0138	0·0138	0	0	0	0·91580
	tra. SLO's, pi loc.	0·19882	0	0	0	0	0	0·87709
cis	SCF	0	−0·0106	0·0351	−0·0090	−0·0163	0·0008	1·0000
	opt. SLO's, pi SCF	0·13904	−0·0086	0·0287	−0·0065	−0·0159	0·0022	0·92148
	tra. SLO's, pi SCF	0·15583	−0·0164	0·0164	0	0	0	0·91312
	tra. SLO's, pi loc.	0·19979	0	0	0	0	0	0·87596

[a] Structure *III*.

dures, where the SLO description is used as a zero order approximation in the computational process of higher accuracy.

The use of localized orbitals within the framework of the many-electron theory, with the aim of simplifying perturbation and configuration interaction treatments, has been discussed many times[30−33]. It was also found possible to use the localized orbitals in one-particle theories. The developed formalism of the perturbation approach to solutions of molecular electronic systems makes use of SLO's as a zero order approximation; as the solution converges practically to Hartree–Fock values after the first iteration step, the method represents an alternative way of solving the SCF problem[28].

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