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Applications of the Group Function Method

IV. CNDO Calculations Using Valence Bond Structures

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The general formulae for wave functions based on separated groups, given in a previous paper, are applied in a CNDO calculation of the ground state energy of a number of simple hydrocarbons and hydrocarbon radicals. It is shown that this approach compares favourably with the usual MO-CNDO method both with regard to the ground state energy and the interpretation in terms of chemical bonding. The results for ethane appear to be in fundamental agreement with the discussion of the origin of the barrier of rotation given by Sovers, Kern, Pitzer and Karplus. Regarding spin densities it turns out that the experimental splitting constants can be reproduced to the same level of accuracy as in the usual MO-CNDO method without using an abnormally low coupling constant.

Key words: Group functions – Valence bond – Barrier of rotation – Spin density

1. Introduction

In recent years molecular orbital (MO) calculations for all valence electrons with complete (CNDO) or intermediate (INDO) neglect of differential overlap are widely applied in the study of problems in organic chemistry [1]. Before the publication of the papers by Hoffmann [2] and by Pople and coworkers [3] MO calculations were usually restricted to π-electron systems only. This apparent hesitation to use the MO method for all valence electrons is not at all accidental. Hückel used his MO calculations to explain the properties of molecules like benzene, where the π-electrons are essentially delocalized, whereas, from chemical experience σ-electrons were thought to be localized in bonds which can best be described by bond functions of the Heitler-London type. This correlation with chemical experience is lost in MO calculations for all valence electrons. In *ab-initio* calculations there is at present no useful alternative for the MO method because of the very severe problems which would otherwise arise from the non-orthogonality of the atomic orbitals and which, despite the growing interest in the VB method, have not yet been solved. These problems, however, do not occur in semi-empirical calculations with neglect of overlap and one might thus conclude that these calculations – if used with care – can be a valuable tool in a test of methods other than the MO approach.

The lack of correlation of MO calculations with chemical experience is of course well known and several methods have been proposed to transform delocalized or "canonical" molecular orbitals into localized molecular orbitals. Such an approach, however, can be dangerous because the localized orbitals depend on the molecule studied, so the chemically interesting interactions become hidden within the actual form of the localized orbitals. Consequently the possibility of a really acceptable interpretation becomes again questionable. A clear example of this problem is the statement [4] that "the additional stabilization that is found in aromatic conjugated systems arises from the fact that even the maximally localized π-orbitals are still more delocalized than the ethylene orbital". This, of course, is not an explanation but rather an alternative formulation of the problem of aromaticity.

In our opinion, methods based on separated electron pairs or more generally on group functions seem to be much more useful. Calculations of this type are usually restricted to one single ground state wave function which is a product of group functions. In many cases, however, an extension to the mixing with other product functions is necessary (in this paper we use the term "product function" to mean a completely antisymmetrized product of bond functions including spin coupling). For example, in a calculation of the spin density distribution in the ethyl radical products of bond functions should be included in which the CH bonds are excited to the triplet state or in which the CH bond functions depend on one or three instead of two electrons. Extensions of this type have been discussed by Kapuy [5], by Diner *et al.* [6] and in the preceding papers of this series [7]. Kapuy's method is based on group functions obtained from a localization procedure as mentioned above, so a comparison with chemical experience is again a difficult problem. In the calculation published by Diner *et al.*, the group functions are taken to be simple products of molecular orbitals. Such an approach has rather bad convergence properties. Moreover, the influence of the chemically interesting bond-bond interactions may become a minor part of the total energy correction.

In this paper we will discuss CNDO calculations of simple hydrocarbons, starting with a wave function which is a product of the "best possible" bond functions obtained from hybridized atomic orbitals. This wave function differs from the wave function obtained from the separated electron pair theory because the bond functions are calculated for isolated bonds. In this way the major part of the bond-bond interactions is introduced through the interaction with other product functions. In this paper we consider the influence of product functions in which part of the bonds are excited and of product functions in which one electron is transferred between two bonds. It will be shown that calculations of this type compare favorably with MO-CNDO calculations with the additional advantage of a simple correlation with chemical experience.

Before discussing the calculations in detail, we will make a few general remarks:

(a) In this paper only molecules will be discussed which, from a chemical point of view, have one single structure. For molecules with essentially delocalized π-electrons like benzene, it may be useful to describe the σ-bonds by the "best possible" bond functions and the π-electron system by simple molecular orbital wave functions. This possibility is easily incorporated into our method. In the same way, a molecule like biphenyl can be described by a number of σ-bonds and by two separated π-electron systems.

(b) All calculations in this paper are based on the CNDO approximation. Upon introduction of the INDO approximation the main difference with our calculations is the fact that matrix elements between the product functions which we will call ψ^G and $\psi_{i,j}^{TT}$ are no longer vanishing. This difference is not important for our final conclusions.

(c) Instead of describing the π-electron system of molecules like benzene by means of a MO wave function, as mentioned above, one may also extend our method by mixing e.g. the two sets of product functions which can be derived from the two Kékulé structures if for both structures the π-bonds are treated in the same way as the σ-bonds. This procedure is in fact a straightforward improvement of the valence bond method introduced in a previous paper on aromaticity and the Woodward-Hoffmann rules [8]. This is rather simple for monocyclic systems. However, for polycyclic systems like naphthalene especially the calculation of matrix elements between charge transfer type of product functions belonging to different sets appears to be very complicated. For this reason we have not considered this possibility in further detail.

2. Outline of the Method with a Simple Example

In this section we will first consider the π-electron system of butadiene. In a simple approximation the wave function for the ground state can be written:

$$\psi^G = \mathscr{A} a_0(1,2)\, b_0(3,4)$$

where $\mathscr{A}$ is the antisymmetrization operator for permutations of electrons belonging to different bonds and $a_0(1,2)$ and $b_0(3,4)$ are general two-electron bond functions for the separated π-bonds A and B. Within an approach as discussed in this paper it is advantageous to use the valence bond method for the calculation of the bond functions. We thus write:

$$a_0(1,2) = \mu_a\{|p\bar{q}| + |q\bar{p}|\}/\sqrt{2} + \lambda_a|p\bar{p}| + \nu_a|q\bar{q}|$$

where p and q are the two atomic orbitals which take part in bond A and μ_a, λ_a, and ν_a are the coefficients of the covalent and ionic terms of $a_0\,(1,2)$.

In order to obtain a complete set of product functions for the 4-electron system, we should also consider product functions in which A or B or both are excited and product functions with a transfer of one or two electrons from A to B or *vice versa*. This leads to the following possibilities:

(a) $$\psi_{ij}(2,2) = \mathscr{A} a\ (1,2)\, b_j(3,4)$$

in which a_i and b_j are either ground or excited state bond functions for A and B. If both bonds are calculated in a basis of two atomic orbitals – as in this paper – this leads to a total number of 9 product functions, including ψ^G.

(b) $$\psi_{a,b}^{TT}(2,2) = \mathscr{A} a_T(1,2)\, b_T(3,4)\,.$$

This is a short-hand notation for the product function in which both A and B are excited to the single one triplet bond function. These triplets are combined to one total singlet by application of the appropriate Clebsch-Gordan coefficients.

(c)
$$\psi^{A,B}_{i,j}(1,3) = \mathscr{A}\, a_i(1)\, b_j(3,4,2)\,,$$
$$\psi^{A,B}_{i,j}(3,1) = \mathscr{A}\, a_i(1,2,4)\, b_j(3)\,.$$

These stand for product functions in which one electron is transferred from A to B or *vice versa*. The resulting doublet bond functions, e.g.:

$$a_i(1) = \mu_i^+\, p(1) + \nu_i^+\, q(1)$$
$$a_i(1,2,3) = \mu_i^-\, |p\bar{p}q| + \nu_i^-\, |q\bar{q}p|$$

are again combined to a 4-electron singlet. Since there are two possible bond functions for both positively and negatively charged bonds, we obtain four possibilities for both $\psi^{A,B}_{i,j}(1,3)$ and $\psi^{A,B}_{i,j}(3,1)$ leading to a total number of 8 product functions.

(d)
$$\psi^{A,B}(0,4) = b(3,4,1,2)\,,$$
$$\psi^{A,B}(4,0) = a(1,2,3,4)\,.$$

Finally, all electrons may be either in A or in B. In a basis of two atomic orbitals for each bond, there is only one possible product function in both cases.

Summing all possibilities together, we obtain 20 product functions, which – as it should be – is the same number as obtained in a VB method including all polar structures or in a MO calculation with complete configuration interaction [9].

For systems with more than two bonds there are of course many other types of product functions. For example in the case of three bonds A, B, and C one of the additional product functions is obtained by charge transfer from A to B, combination of the two resulting doublets to a 4-electron triplet, which together with the triplet of C yields a 6-electron singlet. These highly excited functions will not be considered in this paper, although they will be important for the calculation of excited states.

In most calculations we will restrict ourselves to ψ^G, all product functions in which one of the bonds is excited to the lowest singlet state, all product functions in which two bonds are excited to the triplet state and all product functions with a transfer of one electron between two bonds with both resulting doublets being in their ground state. For n bonds the number of product functions then becomes $1 + n + \frac{1}{2}n(n-1) + n(n-1) = \frac{3}{2}n^2 - \frac{1}{2}n + 1$. In most cases this should be sufficient for a reasonable calculation of the ground state energy. For example in the case of cis-butadiene we obtain, using van der Lugt's parameters [9], for the π-electron energy:

$$\begin{array}{rl} \psi^G \text{ only} & -\;\;9.47\text{ eV}\,, \\ \frac{3}{2}n^2 - \frac{1}{2}n + 1 = 6 \text{ product functions} & -\,10.18\text{ eV}\,, \\ \text{complete calculation} & -\,10.27\text{ eV}\,. \end{array}$$

The matrix elements between the different types of product functions can be calculated in a simple way by using the formulae given in a previous paper [7] or by straightforward application of the rules for matrix elements between valence bond wave functions given by van der Lugt [9]. Therefore we will not discuss this point in detail.

Finally, it should be noted that the functions ψ^{TT} can in general be neglected for ground state calculations on molecules with an even number of electrons. However, they are very important for low-lying excited states. Moreover, we will also use our method for radicals like the ethyl radical, where the unpaired electron is largely localized. In these cases we combine the unpaired electron with an additional electron in a non-interacting "ghost-orbital" to a pseudo-bond-function. Functions ψ_{ij}^{TT} in which either i or j is this pseudo-bond appear to be especially important in calculations of the spin density distribution.

3. Ground State Energies of Some Simple Hydrocarbons and Hydrocarbon Radicals

3.1. General Remarks

In Table 1 we have collected some results of calculations on simple hydrocarbons and hydrocarbon radicals. Before discussing part of these data in detail we first consider some general conclusions.

First of all it appears from the table that in all cases except ethylene rotated over 90° – a special case to be discussed below – the final energy without additional product functions is lower than the value obtained from MO-CNDO calculations. This shows that with regard to the ground state energy our method compares favourably with the usual MO-CNDO approach. What we think to be more important, however, are the conclusions obtained from a comparison of the values given in the different columns of Table 1.

The difference between the energy obtained from ψ^G only and the final value is smallest in the case of the ethane molecule. For planar ethylene this difference is slightly larger, probably because of the change in hybridization. Upon removal of a hydrogen atom these molecules give the ethyl and vinyl radical respectively. In both cases the difference between columns 2 and 3 becomes larger. This is easily understood because the unpaired electron is relatively loosely bound which leads to lower excitation energies of part of the charge transfer type of product functions or, in other words, to a more pronounced delocalization. This same

Table 1. Ground state energies (eV) of some simple hydrocarbons and hydrocarbon radicals

	MO-CNDO	$\langle G \vert H \vert G \rangle$	After diagonalization	+ Additional product functions
Ethane staggered	-511.573	-512.134	-513.439	—
eclipsed	-511.481	-512.116	-513.335	—
Cyclopropane	-705.496	-702.163	-706.983	—
Ethylene planar	-464.318	-464.288	-465.931	-465.931
Rotated over 15°	-464.144	-463.911	-465.734	-465.734
Rotated over 40°	-463.083	-461.735	-464.519	-464.522
Rotated over 60°	-461.547	-458.949	-462.707	-462.737
Rotated over 90°	-458.120	-455.515	-458.032	-459.757
Ethyl radical	-485.116	-484.760	-486.591	—
Vinyl $\angle \mathrm{CCH}_1 = 120^\circ$	-436.394	-434.552	-437.557	—
Radical $\angle \mathrm{CCH}_1 = 150^\circ$	-436.846	-435.168	-437.951	—

effect is observed upon rotation in the ethylene molecule. The π-bond then weakens whereas simultaneously the interaction of ψ^G with the "π-σ"-charge transfer product functions is no longer vanishing for symmetry reasons. Finally cyclopropane is often said to have a more or less delocalized character. This again is reflected in our calculations by the relatively large difference between the values given in columns 2 and 3.

It is furthermore interesting to see that the differences between column 2 and 3 correspond with the differences between the values in column 1, the completely delocalized approach, and column 2, the purely localized picture.

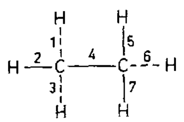
3.2. The Barrier of Rotation in Ethane

Both the MO-CNDO result (0.092 eV = 2.1 Kcal/Mol) and our final result (0.104 eV = 2.4 Kcal/Mol) are in good agreement with the experimental value of 2.9 Kcal/Mol. In the introduction we have remarked that in our method the interaction between the bonds is mainly introduced through the mixing of ψ^G with other product functions. This is clearly illustrated by the very small barrier of 0.4 Kcal/Mol obtained from calculations on ψ^G only. This value is entirely due to the Coulomb-interaction between the isolated CH-bonds. In order to understand the origin of our final value of 2.4 Kcal/Mol we have calculated the contribution of the relevant charge transfer product functions to the ground state energy with second order perturbation theory. From the results given in Table 2 it follows that the charge transfer contribution to the barrier of rotation, as calculated by perturbation theory, is 1.7 Kcal/Mol. Together with the value of 0.4 Kcal/Mol mentioned above, this yields a barrier of 2.1 Kcal/Mol, in good agreement with the complete calculation. It is furthermore interesting to observe the important contribution of the interaction between trans-CH-bonds in the case of staggered ethane.

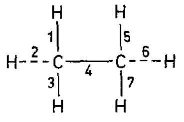
It may be worthwhile to make a comparison of our results with the calculations by Sovers *et al.* [10]. According to these authors the barrier of rotation

Table 2. Charge transfer contributions to the ground state energy of ethane calculated with perturbation theory

CT type of product function	Total contribution for 6 product functions			
	staggered		eclipsed	
	eV	Kcal/Mol	eV	Kcal/Mol
$1 \rightarrow 5$	−0.096	− 2.22	−0.468	−10.80
$1 \rightarrow 6$	−0.096	− 2.22	−0.252	− 5.82
$1 \rightarrow 7$	−0.853	−19.68	−0.252	− 5.82
Total	−1.046	−24.12	−0.973	−22.44



staggered



eclipsed

should be ascribed to the exchange interaction between CH-bonds belonging to different methyl groups. In our case the exchange integrals vanish because of neglect of overlap and differential overlap. It is well known that upon orthogonalization of atomic orbitals the exchange interactions are transformed into interactions between wave functions with a different distribution of electrons over the atomic orbitals. For example, in VB calculations with neglect of overlap polar structures are essential for a description of chemical bonding. In our case these polar structures are replaced by charge transfer type of wave functions. Therefore our results are in fundamental agreement with the conclusions reached by Sovers *et al.*

4. Ethylene

As has been remarked before, the neutral bond $a(1,2)$ is described by the following bond function:

$$a(1,2) = \mu_a\{|p\bar{q}| + |q\bar{p}|\}/\sqrt{2} + \lambda_a|p\bar{p}| + \nu_a|q\bar{q}|,$$

the coefficients μ_a, λ_a, and ν_a being determined by diagonalizing the energy matrix resulting in the eigenvalues of the neutral bond in the ground state singlet, in the first and in the second excited singlet state. The off-diagonal elements of this matrix are proportional to the resonance integral between the orbitals p and q. In the case of ethylene the absolute value of the resonance integral between the $2p_z$-orbitals of the carbon-atoms diminishes upon rotation around the central π-bond and vanishes upon rotation over 90°. This process is accompanied by a reduced energy difference between the first and second excited state resulting in a degeneracy in the case of rotation over 90°. The same holds for the bond-functions, in which the π-bond has one or three electrons, namely:

$$a(1) = \mu^+ p(1) + \nu^+ q(1)$$
$$a(1,2,3) = \mu^- |p\bar{p}q| + \nu^- |qq\bar{p}|$$

respectively.

Therefore in the calculation of ethylene we have taken into account the following additional product functions, describing:

(1) the π-bond with two electrons excited to the second excited singlet state,
(2) the π-bond with one electron excited to the other doublet state,
(3) the π-bond with three electrons excited to the other doublet state.

It appears that after inclusion of the additional product functions our results are again better than those obtained from MO-CNDO. As can be seen in Table 1, the contribution of these additional functions to the energy of the ground state of ethylene is significant only upon a rotation over more than 40°; upon smaller rotations it is negligible. This also gives a justification for omitting these additional product functions in the calculation of the other molecules.

5. The Spin Density in the Ethyl and Vinyl Radicals

As we have remarked before, the wave functions ψ_{ij}^{TT} are important in the calculation of the spin density. E.g. in the case of the ethyl radical the main contribution to the spin density (0.0161) comes from the matrix-elements $\langle\psi_g|\hat{\varrho}|\psi_{ij}^{TT}\rangle$, in which i or j is a pseudo-bond function depending on the unpaired electron and an additional electron in a ghost orbital and $\hat{\varrho}$ is the spin-density-operator. Another important contribution (0.0111) comes from the matrix-elements $\langle \psi_{i,j}(1,3)|\hat{\varrho}|\psi_{i,j}(1,3)\rangle$, in which again i or j is the pseudo-bond. The calculated spin densities for the ethyl- and the vinyl-radical are given in Table 3.

It appears that the MO-CNDO values are about twice our result. In order to make sure that our values are not too low because of product functions not included in the calculation, we have estimated the contribution due to the following matrix-elements obtained from additional product functions by means of a perturbation calculation; in the case of the ethyl radical:

$$\langle \psi_{i^*,j}(1,3)|\hat{\varrho}|\psi_{i,j}(1,3)\rangle$$
$$\langle \psi_{i^*,j}(1,3)|\hat{\varrho}|\psi_{i^*,j}(1,3)\rangle$$

in which j stands for the pseudo-bond and i (i^*) for one of the C–H bonds of the methyl-group with one electron in the lower (higher) lying doublet and

$$\langle \psi_{i,j^*}(1,3)|\hat{\varrho}|\psi_{i,j}(1,3)\rangle$$
$$\langle \psi_{i,j^*}(1,3)|\hat{\varrho}|\psi_{i,j^*}(1,3)\rangle$$

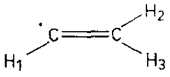
in which i is the pseudo-bond and j (j^*) is one of the C–H bonds of the methyl-group with three electrons in the lower (higher) lying doublet.

The additional spin density, obtained from this calculation is 0.0002, which is negligible.

With the formula $a_H = a \cdot \varrho_H$, in which ϱ_H is the calculated spin density and a is the coupling constant from the Fermi-contact term, we calculated the splitting constant a_H of the hydrogen atoms of the ethyl- and vinylradical. The results are given in Table 3 together with the experimental value. As can be seen in this table,

Table 3. Spin densities in ethyl and vinyl radicals

	Spin density MO-CNDO	Spin density present method	Splitting constant calculated	Splitting constant experimental [11]
Ethyl-radical				
H of the methyl-group	0.0460	0.0277	24.3	26.9
Vinyl-radical ∠ $CCH_1 = 150°$				
H_1	0.0328	0.0204	17.9	15.7
H_2	0.0699	0.0451	39.5	34.2
H_3	0.1160	0.0602	52.7	68.5
Vinyl-radical ∠ $CCH_1 = 120°$				
H_1	0.0745	0.0456	39.9	
H_2	0.0418	0.0242	21.2	
H_3	0.1035	0.0482	42.2	



the MO-CNDO result is too high. In order to find the same splitting constant as found experimentally, the spin densities from the MO-CNDO program have to be multiplied with 506.8 Gauss, while in our calculations the more realistic value of 875.8 Gauss based on an effective nuclear charge of 1.2 has been used.

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