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Bent Bonds, Hybridization, and the Maximum Localization Criterion

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A discussion of the relationship between the concepts of bent bond and hybridization is carried out in connection with the maximum localization criterion (M.L.C.) and the effect of inter-atomic orthogonalization on the direction of hybrids.

Upon introduction of simple constraints on the non-bonding hybrids of water and ammonia derivatives, the M.L.C. gives hybrids practically directed along the bonds. Also inter-atomic orthogonalization of maximum overlap hybrids distorts their contour lines, so that they appear to point more towards the hydrogen atom after orthogonalization than before.

The criteria of definition of hybrids and their relationship to different calculations are briefly discussed.

Die Beziehungen zwischen der Vorstellung der gebeugten Bindungen und der Hybridisierung werden in Verbindung mit dem Kriterium maximaler Lokalisation (M.L.C.) und dem Effekt interatomarer Orthogonalisierung auf die Richtung der Hybride diskutiert.

Wenn man die nichtbindenden Hybride von Wasser- und Ammoniumderivaten einfachen Beschränkungen unterwirft, so ergeben sich mit dem genannten Kriterium (M.L.C.) Hybride, die praktisch entlang den Bindungen ausgerichtet sind. Die interatomare Orthogonalisierung dieser Hybride verändert die Niveaulinien derart, daß die Hybride nach der Orthogonalisierung mehr zu den Wasserstoffatomen hin ausgerichtet sind als vorher.

Es werden Kriterien der Definition von Hybriden und ihre Beziehung zu verschiedenen Rechnungen diskutiert.

L'article présente des considérations sur le concept de liaison courbe et l'hybridation, en relation avec le critère de localisation maximum et l'effet de l'orthogonalisation intératomique sur la direction des hybrides.

Des conditions très simples sur les hybrides non liantes des dérivés de l'eau et de l'ammoniaque donnent lieu à des hybrides liantes qui sont pratiquement dirigées le long des liaisons. L'orthogonalisation à la Löwdin des hybrides obtenues par le critère du recouvrement maximum produit une distortion des courbes de niveau telle que les nouvelles hybrides sont essentiellement dirigées le long des liaisons.

Les différents critères de définition des hybrides selon le type de calcul sont discutés.

Introduction

In previous papers [*1*, *2*, *3*] we proposed a method for determining a basis of hybrid orbitals which would be adapted to a treatment of σ systems involving, as a preliminary step, the determination of localized bond orbitals. That method introduced a "maximum localization criterion" which was shown to amount to the requirement that the hybrid orbitals of different atoms should overlap as little as possible with one another unless they correspond to actual bonds in the chemical sense (including many-centre bonds).

The method appeared to be very satisfactory for hydrocarbons [*2*, *3*], whereas, as was noted at the end of Ref. [*2*], it gives seemingly surprising results for molecules containing heteroatoms. For instance, the bonding hybrids of oxygen of water appear to have a high *s*-character, so that they form an angle much larger than the bond angle (138° and 105°, respectively). This may be taken as an indication that the bonds of water are "bent", and that bent bonds are a feature common to most systems containing heteroatoms. Actually, whether the bonds are "bent" or not, depends on the definition of a bond, on the hybrids used to give an LCAO picture of it, and on the coefficients with which they enter into the bond orbital: therefore, conclusions drawn only from the hybrids are highly questionable. However, in the present paper, we shall accept, in order to clarify certain points regarding bent bonds and their definition, the current idea that a bent bond arises whenever one or both the hybrids forming the bond are not directed along the line joining the two atoms participating in it. One can easily find arguments to show that the conclusion that bent bonds, in this restricted sense, are very common is not as unrealistic as it appears at first sight [*2*, *4*]; nevertheless, in Ref. [*2*] we have only pointed out that the maximum localization criterion leads to bent bonds just if it is strictly limited to bond overlaps, i.e. if no restriction is imposed on non-bonding hybrids, but for the orthogonality condition.

Now, this complete flexibility of the non-bonding hybrids is not entirely satisfactory for several reasons: in particular the use of overlap for determining the hybrids is the effect of a drastic, if reasonable simplification. In fact, the matrix one actually intends to treat is the Hamiltonian matrix, which depends also on the populations of the various atomic orbitals: a new formulation of the maximum localization method taking the populations explicitly into account can in fact be obtained [*5*]. However, for a discussion of the definition of bent bonds in terms of hybrids, it is sufficient to treat the question semiempirically.

This is what we shall do in the present paper, which is intended to throw some light on two questions:

a) Does the maximum localization criterion, when non-bonding hybrids are treated in an appropriate way, give practically straight bonds in the sense specified above ?

b) Even if only overlap is used to determine the optimum hybrids, and hence bonds appear to be bent, are apparent contradictions with calculations indicating that bonds are straight necessarily genuine, or are they vitiated by differences in definition of hybrids ?

We shall consider in detail point (a), for its discussion involves a procedure which may be useful for general applications of our method; as to point (b) we shall illustrate it in the discussion.

General Considerations

The method of Ref. [*1*] consists in finding for each atom A some preliminary hybrids satisfying the maximum localization criterion, but not orthogonal to one another, and then finding a set of orthogonal hybrids by imposing a condition involving certain weights $\lambda^2_{X_i}$. These weights are taken equal to the highest eigenvalues of the matrices $S_{\mathrm{AX}_i} S^{\dagger}_{\mathrm{AX}_i}$, S_{AX_i} being the overlap matrix between the orbitals of atom A and those of the atom X_i, which forms with A the bond in which the i-th hybrid of A is supposed to participate. When the atom A forms less than four bonds, the hybrids not participating in bonds are not specified in the preliminary choice, for they are assigned weights $\lambda^2_{\text{sol}} = 0$ in the orthogonalization procedure. This choice of λ^2_{sol} (which will be denoted just by λ in the following) is perfectly reasonable as long as maximum intra-bond overlaps are required; however, the complete flexibility of the non-bonding hybrids referred to before and introduced by the choice of $\lambda = 0$ may not be the best if one refers to the original purpose, namely the approximate factorization of the eigenvalue equation according to the chemical bonds, although the approximation from which it stems (off diagonal elements of the Hamiltonian matrix H proportional to the corresponding overlap integrals [*1*]) is quite reasonable [*6*]. In particular, one could take into account, when considering possible restrictions for non-bonding hybrids, the fact that the diagonal elements of the intra-atomic bonds of the Hamiltonian matrix H are different for the $2s$ and the $2p$ orbitals: those for the former are usually higher in absolute value than those for the latter.

Emphasis on this point has already been placed by Certain et al. [*7*] who determined hybrids by the criterion of maximum total overlap, which has some similarity to our method, although it is not directed explicitly towards the problem of localization. The Authors of Ref. [*7*] write: "The foregoing remarks are not intended to desparage the MOO method. On the contrary, it is felt that the agreement obtained between the calculated and observed values of the ^{13}C–H coupling constants and HCH bond angles in this study is quite encouraging to further inquiry. The point stressed here is that the method might be improved if an additional constraint, reflecting the effects of rehybridizing the non-bonding electrons, were added to the original requirement that S_{total} be a maximum. Pauling has suggested the use of the s-p promotional energy for a rather similar purpose. Such an approach, although it appears to neglect the compensating energy gained through rehybridization of the bonding orbitals, may provide a basis for the needed modification".

The above considerations, applied to the method of maximum localization, suggest that a simple way to treat the non-bonding hybrids would be to suppose that the intra-atomic blocks H_{AA} of H play, with respect to them, the same role as the overlap matrices S_{AX_i} play with respect to the bonding hybrids: namely, that they should be used to determine the weights and forms to be assigned to the non-bonding hybrids before orthogonalization. As regards the latter, we may reasonably assume that the initial non-bonding hybrids correspond to pure $2s$ orbitals, for this is the case if H_{AA} is supposed to be diagonal; as regards the weights, however, one should know both the elements of H_{AA} and some proportionality constant corresponding to the ratios between the off-diagonal elements of H and those of the overlap matrix S. Given the present state of σ system calculations, such a procedure would be necessarily empirical: we propose, therefore, to take directly λ as an empirical parameter. This is entirely justified, from our point of view, for the question we wish to answer here is just the following: is it possible to determine a single λ for a given hetero atom, so that a whole series of molecules containing it may have straight bonds (as opposed to bent bonds in the sense specified above)?

Calculation and Results

The calculations have been carried out using the programs already employed in Ref. [*2*]. Those programs allow the introduction of arbitrary weights for the various orbitals; therefore, we have been able to vary the weight λ of the lone-pair hybrids from 0 to 0.5, in the molecules of water and ammonia, so as to plot the angles between the bonding hybrids *vs.* the weight in question. The diagrams obtained show that the value $\lambda = 0.25$ gives angles between the bonding hybrids practically equal to the experimental bond angles [*8*], both in ammonia and in water. The hybrids of oxygen and nitrogen corresponding to that value of the weight λ are reported in Tab. 1 and 2. As a consequence of having chosen pure $2s$ orbitals to represent the non-bonding hybrids before orthogonalization, the final form of these hybrids appears to have a much higher s-character than the same hybrids have when they are assigned weight 0. We also note that, when the weight of the lone-pair hybrids is 0.25, the non-bonding hybrids of oxygen are oriented so as to be equivalent, whereas, when the same weight is 0, one of them is a pure p orbital, and the other lies in the HOH plane (although, of course, they can be linearly combined so as to make them equivalent).

Table 1. *Hybrids of oxygen in water corresponding to the case when the angle between the bond hybrids is equal to the bond angle; each hybrid has the form:* $h = a(2s) + b(2p_z) + c(2p_x) + d(2p_y)$. *The choice of the reference system and the coordinates of the atoms are indicated in Tab. 3*

	h_1	h_2	h_3	h_4
a	0.4526	0.4526	0.5433	0.5433
b	0.0	0.0	0.7071	0.7071
c	0.5433	0.5433	−0.4526	−0.4526
d	0.7071	−0.7071	0.0	0.0

Table 2. *Same as Tab. 1 for nitrogen in ammonia*

	h_1	h_2	h_3	h_4
a	0.4808	0.4808	0.4808	0.5537
b	−0.8768	0.2585	0.2585	0.3124
c	0.0	0.7071	−0.7071	0.0
d	−0.0010	0.4495	0.4495	−0.7719

Table 3. *Co-ordinates, bond angles and bond lengths in water and ammonia*

	water			ammonia			
	O	H_1	H_2	N	H_1	H_2	H_3
x	0	.587	.587	0	0	.814	−.814
y	0	.757	−.757	0	0	.529	.529
z	0	0	0	0	−1.014	.293	.293

H–N = 1.014 Å; $\widehat{HNH}$ = 107°; H–O = 0.958 Å; $\widehat{HOH}$ = 105°.

Also the atomic moments of the lone-pair hybrids are completely different in the two cases: the increase in the s-character of the lone-pair hybrids induced by the new choice of λ leads to an increase of this quantity, and therefore to an increase of the total atomic moment, which is evidently equal to that of one electron per doubly occupied hybrid. For instance, when $\lambda = 0$, the total atomic moment of ammonia is 0.996 D, whereas it is 1.762 D when $\lambda = 0.25$.

In order to answer question (a) formulated at the end of the introduction, we have adopted the above-mentioned values of the weight of the non-bonding hybrids for determining the new hybrids of the methyl derivatives of water and ammonia. In particular we have studied methyl alcohol, dimethyl ether, methylamine, dimethylamine, and trimethylamine. The geometries were taken from Ref. [*8*]. The results, obtained using the overlap integrals given in Ref. [*9*], with orbital exponents according to Ref. [*10*], are summarized in Tab. 4.

Table 4. *Angles between the bonding hybrids and s-characters of the non-bonding hybrids for the methyl derivatives of water and ammonia, with different weights of lone-pair hybrids of oxygen and nitrogen, respectively*

compound	atoms	(a)	(b)	(c)	(d)	(e)
H_2O	$\mathrm{H\hat{O}H}$	105°	138°	(105°)	0.077	0.295
CH_3OH	$\mathrm{C\hat{O}H}$	108°	136°	103°	0.083	0.310
$(CH_3)_2O$	$\mathrm{C\hat{O}C}$	111°	134°	103°	0.089	0.321
NH_3	$\mathrm{H\hat{N}H}$	107°	116°	(107°)	0.073	0.306
CH_3NH_2	$\mathrm{C\hat{N}H}$	109° 27′	115°	107°	0.065	0.303
$(CH_3)_2NH$	$\mathrm{C\hat{N}H}$	109° 27′	117°	108°	0.072	0.324
$(CH_3)_3N$	$\mathrm{C\hat{N}C}$	109° 27′	116°	107°	0.080	0.347

(a) Bond angles used for determining the coordinates of the nuclei. The angles for the first four compounds are taken from Ref. [*8*], within ±1°. For the last three compounds a tetrahedral angle has been chosen for the sake of simplicity*.

(b) Angles between bonding orbitals with $\lambda = 0$.

(c) Idem, for $\lambda = 0.25$. The parentheses for water and ammonia indicate that the corresponding angles served to determine the value of λ (see text).

(d) s-character (value of a^2, Tab. 1) of non-bonding hybrids with $\lambda = 0$.

(e) Idem, with $\lambda = 0.25$.

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* It is likely that the experimental CNH angle in methylamine is closer to 112°; however, especially in view of the comparison between the three amines, we have preferred the lower value. In any case the argument this table illustrates does not rest upon the agreement between the angles given in column (a) and observed values, but on the comparison between column (a) and column (c).

Discussion

The results given in Tab. 4 show that an appropriate choice of the weight given to the lone-pair hybrids in the frame of the method of Ref. [*1*] leads to angles between the bonding hybrids that are in much better agreement with the experimental bond angles than those obtained by choosing a weight equal to 0. The change of the angle between the bonding hybrids, when one passes from one case to the other, is much more marked for the oxygen derivatives than for the derivatives of ammonia. This can be attributed to the fact that oxygen has two lone pairs, for it cannot depend on the choice of the weight λ, which is the same in both cases. This is an encouraging conclusion, for it shows that the procedure used here takes correct account of the number of non-bonding hybrids. Tab. 4 also shows that the angles obtained when the weight is 0.25 tend to be smaller than the observed angles, whereas those calculated with zero weight are larger. This is very important, for it is easier to explain on the basis of Van der Waals and electrostatic repulsions (c.f. [*4*]) bonds which are slightly bent inwards than bonds bent outwards.

Coming back to question (a) of the introduction, we can thus state that the answer to it is positive, although the simplification involved in having chosen the same λ for a whole series of compounds did not allow us to obtain strictly straight bonds.

As regards question (b), we emphasize, first of all, that the bonds found by the present procedure are still slightly bent and that the introduction of a λ different from zero somewhat betrays the original purpose of maximizing the interatomic elements of H and S corresponding to chemical bonds; these facts indicate that the basic problem to which the present paper relates, namely the relationship between hybrids and "bent bonds", is only partly solved by the proof here presented that an appropriate choice of the lone-pair weight can lead to much more reasonable valence angles. In fact, all we can say so far is that, as long as one accepts the definition of a bent bond given in the introduction (hybrids not directed along the line joining the atoms participating in the bond), the only case where a basis consisting only of L-shell Slater orbitals necessarily leads to bent bonds is that of cyclic hydrocarbons.

However, we emphasize here that, even within that definition, the whole question of bent bonds hinges upon the criterion and the purpose of the introduction of the hybrids. For instance, one might be interested in applying to a system of σ bonds the formalism of group product functions proposed by McWeeny [*11*] without introducing the somewhat delicate "strong orthogonality condition"; for this condition involves the use of orthogonalized (i.e. delocalized!) atomic orbitals. In such circumstances, one would be interested in having as small as possible an overlap between the various bonds to be treated as "groups". Therefore, one should probably use hybrids defined according to the maximum localization criterion of Ref. [*1*] based exclusively on overlap, so as to minimize inter-bond overlaps; the weight assigned to the lone-pair hybrids should then be 0, even if this seems to introduce bent bonds in the sense specified above.

On the other hand, if the hybrids are introduced in the frame of a calculation involving orthogonalization by the procedure suggested by Löwdin [*12*], it may very well happen that the delocalization thus introduced masks the fact that the corresponding purely atomic hybrids are not directed along the bonds. This remark is interesting in connection with a study of water [*13*] made according to Ref. [*11*]. There the Author reaches the tentative conclusion that it is not necessary to introduce bent bonds in describing water; and infers from this that a definition of hybrids based solely on overlap is unsatisfactory. The latter inference is certainly correct if it is taken together with the peculiar features of the method used in Ref. [*13*]; but if it were considered as a general result, it would correspond to an arbitrary identification of orthogonalized orbitals with localized atomic orbitals.

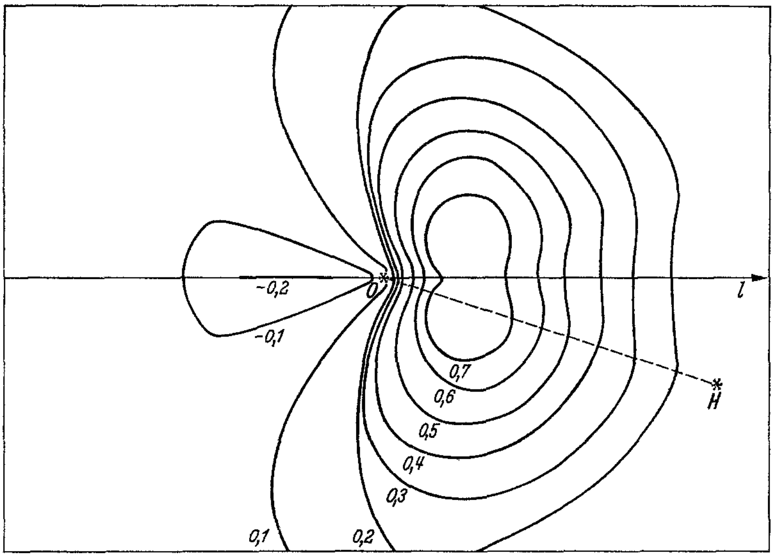

Fig. 1. Contour lines of the maximum overlap hybrid of oxygen in water

In order to show clearly the danger of confusion arising from ignoring the effects of orthogonalization, so that apparently similar definitions of bent bonds lead to contradictions which might be removed by a deeper analysis of the situation, we present the diagrams of Figs. 1 and 2. Fig. 1 shows the contour lines of a hybrid of oxygen in water obtained by maximizing the overlap associated with an OH bond; this hybrid, as has been mentioned, points in a direction forming an

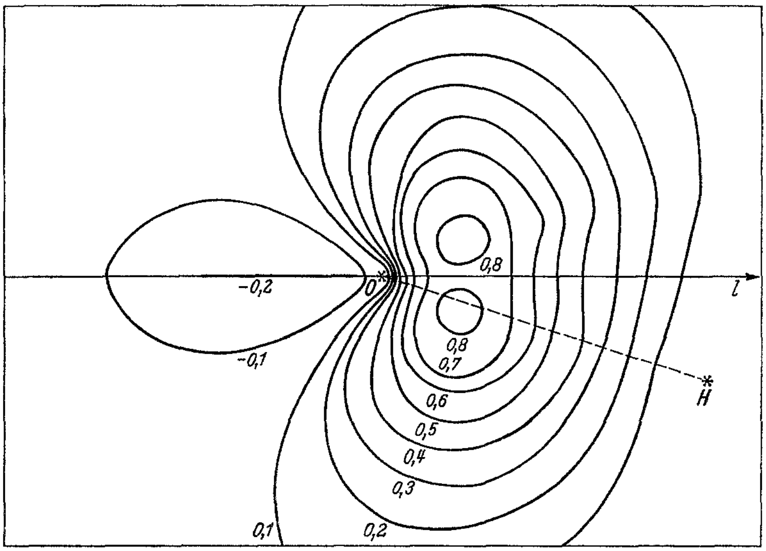

Fig. 2. Contour lines of the hybrid of Fig. 1 after orthogonalization to the 1*s* orbital of hydrogen by the Löwdin procedure. The expectation value of the vector $\vec{r}$ for the orthogonalized hybrid shown forms an angle of $\approx 1^0$ with the OH line

angle of 18° with respect to the OH line. Fig. 2 shows the contour lines of the same hybrid orthogonalized by combination with the $1s$ orbital of hydrogen by the procedure of Ref. [*12*]. The distortion obtained in the latter case is significant, and shows how a combination with the $1s$ orbital can distort the original hybrid so as to make an identification between the two definitely unsatisfactory.

Conclusion

As has been stated in the introduction, the problem of defining bent bonds is much more complicated than has been thought so far; in particular, the current definition based on the direction of the hybrids is a very special one, and probably needs revision. However, the soundest procedure for reaching a new definition requires, in our opinion, a careful analysis of the old one. The present paper has been written in this spirit.

The conclusions reached are the following:

a) considerations based on energies can lead to a modification of the maximum localization criterion for defining atomic hybrids, so that the latter point in the direction of the bonds in many cases where hybrids defined by the same criterion applied only to overlap do not;

b) hybrids of the latter type can be necessary for certain types of calculations, which require at least approximate bond-bond orthogonality, and are often to be preferred to hybrids determined according to more complicated considerations;

c) conclusions about bent bonds in the sense of the current definition derived from calculations involving orthogonalization do not necessarily apply to fully atomic hybrids, and should be interpreted as involving a new definition of bent bonds.

We add that the whole problem of hybridization and bent bonds is also connected to the choice of the pure-orbital basis: the use of a small truncated set of Slater orbitals introduces hidden empirical features in most calculations, in particular as regards overlap [*6*]. Therefore, it should be examined in connection with the use of an extended basis.

Finally, we emphasize that quantum mechanically hybridization is just a unitary transformation of a given basis intended to give a particular form to the overlap matrix and to the Hamiltonian matrix, namely to maximize as far as possible certain elements of them; therefore, apart from the question of bent bonds, the very question of deciding which are the true hybrids in an absolute sense is meaningless, and so are discussions on it: the problem is rather to decide what kind of hybridization leads to a description of a σ-system which is simpler: one criterion could be that of trying to obtain a description in terms of localized bond orbitals mixing with one another as little as possible, as was done in Ref. [*1*]; other criteria derive from differents points of view [*14*]. What should be common to all of them is the attempt to introduce concepts and definitions which, as RUEDENBERG says in a very profound analysis of this question, can "contribute to bridging the gap between chemical concepts and rigorous mathematical treatments" [*14*].

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