

Pauling's Hybridization as a Tool of Computational Chemistry

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Hybrids were introduced by Pauling within the Valence Bond method on intuitive grounds a long time ago. For the last thirty years, as a result of shift of interest towards computations based on the Molecular Orbital method, hybrids have been neglected by most theoreticians. In this paper, we show that actually they are not only deeply rooted in molecular reality (because of their connection with directed valency) but can be used to process the enormous output of sophisticated molecular computations, so as to derive from them the information needed for such research as the establishment of general rules and the description of the electronic systems of large molecules. Localization, lone pair hybrids, bent bonds, and related topics are discussed starting from *ab initio* computations either as single canonical orbitals or as Fock and overlap matrices. Our »maximum localization« procedure for constructing hybrids, which is close to maximum overlap procedures, appears to yield localized orbitals as good as those obtained from other localization criteria, with the advantage that the hybrids are always directed along the bonds as much as this is allowed by valence angles. The »straight bond« criterion for constructing a reaction path starting from a strained situation is briefly recalled as an indication that Pauling's discovery of hybridization still has a large unexploited potential.

INTRODUCTION

Sixty years ago, Linus Pauling introduced hybridization into the world of the newborn quantum chemistry.¹ Thirty years later, Per Olov Löwdin used to speak affectionately of the »Pauling point« in the evolution curve of quantum chemistry, referring at the same time to the successes of Pauling's intuitive approach, firmly rooted in facts, and to its resistance to a formal translation into a rigorous quantum mechanical for-

mulation. This happened at the dawn of computational chemistry, whose successes have been surprising to many. Unfortunately, scientists of the younger generation seem to have completely forgotten the Pauling point, and have somewhat disappointed those who hoped that computational chemistry would bring theory back to it after shaping the tools for making Pauling's unsurpassed intuitions rigorous and quantitative. A few computational chemists even smile at such notions as »orbital«, »hybrid«, »electronegativity«, *etc.*; yet they should be able to realize from what they learned in undergraduate studies that rules involving these concepts are the guidelines for making order in the overpopulated world of organic and metal-organic molecules, and that they provide the kind of theory experimental chemists want. The Nobel prize awarded to the »semi-empiricists« R. Hoffmann and F. Fukui in 1982 is perhaps the most striking indication of this.

Hybridization served to construct the theory of directed valency in the context of a Valence Bond approach to the quantum treatment of electrons in a molecule; but the transfer to the now ubiquitous Molecular Orbital scheme was made by Mulliken himself, though after much hesitation.² After him several researchers, to whom reference will be made later in this paper, worked at an accurate mathematical formulation of the criteria for optimum hybrids within an MO scheme, but little use was made of their studies. It is perhaps due to the fact that the transfer to the MO scheme had not been fully appreciated that brilliant researchers like Roald Hoffmann constructed their semi-empirical MO methods without taking any account of hybridization, so that even they did not go completely back to the Pauling point.

In this paper we try to use previous studies on hybridization to provide examples and guidelines for a task that seems most urgent in the spirit of the above reflections, namely the processing of the output of accurate molecular computations aimed at the ordinary chemist. The urgency of this task stems from (I) the fact that now the time seems ripe for applying computational chemistry not only to spectroscopy, but to chemical problems, such as reactions involving comparatively large molecules, or even macromolecules, and (II) the fact that computational chemistry is now turning to vibrational analyses and time evolution studies,³ so that electronic wave-function studies are in serious danger of remaining at the stage of black-box programmes intended for non-specialists, and yet including little or no application-oriented processing of the output.

We shall concentrate on two problems: (I), how to recast a Canonical Molecular Orbital (CMO) into a simple form, involving *ad hoc* hybrids, and (II), how to construct general hybrids, starting from the results of *ab initio* computations. For a general critical background of the following study the reader is referred to our previous papers, in particular ref. 4.

A. HYBRIDIZATION AND LOCALIZATION

In this paper, we refer to hybrids (or hybrid orbitals) in the usual chemical sense (whereas physicists use the same word for band mixing), *viz.* as linear combinations of atomic orbitals with different angular quantum numbers and (usually) of the same size belonging to the same atom:

$$|h\rangle = N (a|s\rangle + b_1|px\rangle + b_2|py\rangle + b_3|pz\rangle) \quad (\text{A. 1})$$

As it is well known, when only s and p AO's are involved, this hybrid can always be written in the form of an sp^n hybrid:

$$|h\zeta\rangle = (|s\rangle + n^{1/2} |p\zeta\rangle) / (1 + n)^{1/2}, \quad (\text{A. 2})$$

where $|p\zeta\rangle$ denotes a p orbital symmetric with respect to the axis ζ defined by the three p components of eqn. A1. The d, f, \dots components of eqn A1 destroy the axial symmetry of a hybrid so that, in general, its »direction« is no longer given by the axis ζ of the p components. In this case, the »centroid« of the hybrid, whose coordinates are given by $\langle h|x|h\rangle$, may serve to determine a direction and a sign.

The highly directional properties of combinations, such as eqn A1, make them important not only in the elementary theory of valence, where form A2 is most current, but in more sophisticated theoretical analyses, as it will be illustrated below. Moreover, since directionality is tantamount to polarization, it is customary to consider the formation of hybrids, *i.e.* *hybridization*, as a sort of physical response of an atom to the perturbation produced by other atoms.

A formal discussion of hybridization in the context of the Molecular Orbital Model of molecules is strictly dependent on the notion of localization. It is important to discuss this point briefly.

Within the Born-Oppenheimer approximation, a molecule can be described as a system of point masses (the atoms) held together by three types of interaction:

- two-centre σ bonds, which can be thought of as springs connecting one atom to the other in a way largely independent of the rest of the molecule;
- many-centre σ bonds;
- two- and many-centre π bonds.

Although many quantum chemists now dispense with this picture, attempts to find its counterpart in the description of a molecule as a system of electrons in the field of fixed nuclei, which go back to the dawn of quantum chemistry, are still of great interest because experimental chemists continue to base their research on a model of molecules involving a quasi-rigid system of localized bonds, each holding two atoms together, and a system of additional, possibly conjugated bonds. Additive rules for physical properties (*e.g.* geometries, electric dipole moments, force constants, *etc.*) and reaction mechanisms provide extensive proof that the »elementary« description is a powerful research tool.

The main attempts at making molecular-orbital computations match the basic model started with the notion of localization. Several criteria and methods have been proposed, generally conceived as linear transformations of given canonical MO's - which we shall call *a posteriori* localization inasmuch as it requires knowledge of computed molecular orbitals. We recall here the most popular procedures:

- the methods of Edmiston-Ruedenberg⁵ and of von Niessen⁶, both based on the localization of electron densities. The former maximizes the repulsion energy between doubly occupied molecular orbitals, the latter minimizes the overlap charges in each molecular orbital;
- the method of Boys-Foster,⁷ which reaches the same result by maximizing the sum of the squares of the distances between the centroids of the various orbitals;

– the method of Magnasco-Perico,⁸ which maximizes the sum of the local Mulliken electron populations in the subspaces corresponding to the bonds, lone pairs, and atom cores.

The above illustrate the whole class of *a posteriori* localization methods. The first two are examples of what Daudel *et al.*⁹ call the »internal« localization criterion, inasmuch as they are attempts to »discover« the bonds in a canonical orbital description of molecules by associating them with some physical quantity. The third criterion belongs to the class the same authors would call »external«, since it »defines a correspondence between the orbitals and the regions of space« where they are to be localized.

In this context hybridization is a further step, being an attempt to describe the localized orbitals in terms of one atomic orbital per atom. If this is done, then hybridization is seen as a distortion of the valence atomic orbitals resulting from bond formation but is not considered as a factor determining binding itself, in particular its geometrical properties. So much so that in certain cases (*e.g.* water in the Ruedenberg-Edmiston scheme) the »hybrids« are not directed along the bonds. Nevertheless, they can be useful as tools for discussing *ab initio* localized (and even canonical) molecular orbitals, as it will be shown later. As an example of *a posteriori* hybrids we mention here only the »natural hybrids« of Foster and Weinhold,^{10,11} derived from Löwdin's natural orbitals obtained from a given first-order density matrix.

A priori localization consists of a choice of the basis atomic orbitals to be used for subsequent molecular orbital determinations such that the Hamiltonian matrix may be expected to be approximately factorized into diagonal blocks corresponding to lone pairs, two-centre bonds, *etc.* In this frame it is easier to grasp the importance and significance of hybrids, because they arise as a natural formalization and extension of the elementary theory of directed valency. Here, the idea is that computations of any degree of accuracy and sophistication will be carried out on a preliminary MO description of the molecule that strictly follows the above classification of bonds. Therefore, ideally, one defines two-centre σ orbitals, many-centre σ orbitals, two- and many-centre π orbitals, leaving the specification of the LCAO form to computations of the level desired. Localization then consists in applying criteria that lead to a group of such orbitals optimal for a given molecule and amounts to the preparation of a *hybridized atomic orbitals basis* (HAO basis) specific of the given molecule. Consider, for simplicity, a minimal HAO basis (*i.e.* a basis consisting of HVAO's hybridized *valence* atomic orbitals) and a localized σ bond between first- or second-row atoms. This will be described by a molecular orbital consisting only of two basis orbital, one hybrid per atom, directed towards one another, as in the elementary theory of valence. In the latter, however, the HAO's are normally taken to be sp^n hybrids with $n = 0,1,2,3$, whereas the optimization implied by the above definitions may lead to fractionary n -values in eqn A1, thus extending the scope and the significance of Pauling's original proposal. The reason why use of just one orbital per atom is possible is that the four valence orbitals of each atom are so combined with one another that out of the four resulting combinations just one has a significant interaction with just one analogous combination of the partner in the bond. This may be mathematically formulated as the application of a block-diagonal unitary transformation T to the original AO basis such that only orbitals of the same atom are mixed together.

Several procedures have been proposed for constructing *a priori* hybrids not limited to integral n values.

- adjustment to molecular geometry, under the orthogonally constraint:^{1,12}
- Mulliken's maximum overlap method¹³ (calculation of overlap integrals as functions of the hybridization coefficient and of the interatomic distance);
- the maximum overlap method of Murrell,¹⁴ who was the first to take into account the effects of atoms bound to a single central atom in molecule MX_k. This method was later used by a number of other authors.¹⁵
- maximum localization criterion.¹⁶ This method computes in a simple manner those hybrids which ensure the highest localization in the direction of the bonds that each atom forms with atoms linked to it, working on 4x4 matrices (for an s-p basis) and imposing only normalization and orthogonality conditions.
- the density matrix method of McWeeny and Del Re,¹⁷ where the atomic orbital basis is hybridized in such a way that the molecular orbitals associated to a given (possibly SCF) Hamiltonian yield a density matrix as close as possible to a specific localized form (2x2 diagonal blocks for bonds, 1x1 diagonal blocks for lone pairs, etc.).

In all cases, the hybrids obtained are similar, and correlations have been found with CC and CH NMR coupling constants, stretching frequencies, bond electric dipole moments, thermodynamic acidity constants.¹⁸

In the following sections, in accordance with the aim mentioned in the introduction, we will try to show how the two procedures for determining hybrids can be applied and used for obtaining numerical pictures of orbitals and bonds that are simple and susceptible to direct interpretation in terms of physical effects. Our point of view is that the construction of such a simple picture is a necessary step if computational chemistry is to be made into a chapter of the theory of molecular structure interesting to the experimental organic chemist.

B. A POSTERIORI HYBRIDIZATION

In this section we make an attempt to substantiate the claim already made that the direct analysis of molecular orbitals in terms of hybrids can be a useful tool for processing the output of large-basis *ab-initio* computations, whose results are the less visualizable in terms of chemical concepts the more accurate they are. We will pause on the extreme example of the »*a posteriori*« analysis applied to canonical molecular orbitals rather than to localized orbitals issued therefrom.

In this case, hybrids allow the investigation of localization not by imposing it as it is done in the procedures listed above but as a possible property of the canonical orbitals. In spite of serious limitations (*e.g.* the impossibility of applying it to symmetrical molecules), this approach is conceptually fundamental, and is especially interesting in the case of large molecules, particularly biomolecules, and metal clusters, where different binding regions exist.

This point can be illustrated by a study of the systems modelling enzymatic sites characterized by one or two H-bonds, recently carried out by us.^{19,20}

In order to represent a canonical molecular orbital (CMO) in terms of hybrids, it is necessary to reduce it to a linear combination of one »*in situ* Modified Valence Atomic Orbital« (MVAO^{13b,21}) per atom. This can be done by a number of steps, which amount to isolating the 1s contribution and expressing the contributions of higher quantum numbers by means of new basis atomic orbitals. The latter are derived from the given CMO by normalizing the linear combination of the basis orbitals associated

to a given principal quantum number and then Schmidt orthogonalizing it to the lower atomic orbitals of the same atom and same angular species, obtained in the same way.²² These steps are illustrated here on simple examples; the reader can consult ref. [22,23] for a general formulation.

First of all, the 1s contribution is isolated. Then, the contributions of higher atomic orbitals are determined from the pertinent coefficients C_{μ} in the given CMO by normalizing the linear combination of the basis orbitals associated to each principal quantum number. In the case of a 2s orbital resulting from a double-zeta basis, this gives the following expressions for the contracted AO $|2s'\rangle$ and its coefficient $C_{2s'}$ in the CMO:

$$|2s'\rangle = (C_{2sI} |2sI\rangle + C_{2s0} |2s\rangle) / C_{2s'} \quad (\text{B.1})$$

$$C_{2s'} = k \text{ SQR}(C_{2sI}^2 + C_{2s0}^2 + 2C_{2sI}C_{2s0} \langle 2sI|2s0\rangle), \quad (\text{B.2})$$

where k is the sign of the C_{μ} that is larger in magnitude. Similar expressions hold, of course, for the p AO's.

Each contracted AO's is then Schmidt-orthogonalized to the lower orbitals of the same atom and same principal quantum number. In our example, we thus obtain the final *in situ* $|2s\rangle$ AO for the given CMO and the pertinent coefficient from the expressions:

$$|2s\rangle = N (|2s'\rangle - |1s\rangle \langle 1s|2s'\rangle) \quad (\text{B.3})$$

$$N = \text{SQR}(1 - 2 \langle 1s|2s'\rangle^2 + \langle 1s|2s'\rangle^4); \quad (\text{B.4})$$

$$C_{1s} = C_{1s}^0 + C_{2s'} \langle 1s|2s'\rangle;$$

$$C_{2s} = C_{2s'} (1 - \langle 1s|2s'\rangle^2)$$

where C_{1s}^0 is the original coefficient of the 1s orbital; the new coefficient being practically zero, because of the separation of the K and L shells.

Finally, the s and p components are contracted so as to provide a single HAO to which a single coefficient is assigned in the given CMO:

$$|h\rangle = a |2s\rangle + b_x |2px\rangle + b_y |2py\rangle + b_z |2pz\rangle; \quad (\text{B.5})$$

$$c_h = k \text{ SQR}(C_{2s}^2 + C_{2px}^2 + C_{2py}^2 + C_{2pz}^2) \quad (\text{B.6})$$

In the case of the HOMO of the propeniminium ion-ammonia system (I, Figure 1), these steps yield the results shown in Table I.¹⁹

This procedure reduces the given CMO to a linear combination of one hybrid MVAO for each atom and each (nlm) quantum number set. Thus, the CMO takes the form of a linear combination of one HMVAO per atom and per principal quantum number. In principle, if the principal quantum number n corresponding to the valence orbitals of the free atom is given, it is also possible to include polarization functions in the treatment. In the example of Table I the HOMO of system I is approximately reduced to the form

$$|\psi\rangle = -0.2444 |h(N_p)\rangle + 0.9333 |h(N_a)\rangle,$$

where h denotes the pertinent hybrid reported in the last line of Table IB for the nitrogen atom indicated. Such a representation would allow detection of the lone pair

TABLE I

Processing of the contributions of the H-bridge nitrogen atoms (N_p and N_s) to the double-zeta (4-31G ab initio) canonical HOMO of the propeniminium ion-ammonia (I, Figure 1)

A. Coefficients of the basis AO's in the HOMO and intra-atomic overlap integrals ^a					
	N_p	N_d			
1s	0.0282	-0.0540		$\langle 1s 2sI \rangle$	= 0.1971
2sI	-0.0321	0.0957		$\langle 1s 2sO \rangle$	= 0.1696
2pxI	0.0571	0.0578		$\langle 2sI 2sO \rangle$	= 0.7759
2pyI	0.0997	0.4634		$\langle 2pI 2pO \rangle$	= 0.5196
2sO	-0.1306	0.2099			
2pxO	0.0563	0.2429			
2pyO	0.1103	0.4436			
B. Expansions and coefficients of the orthogonalized contracted ^b AO's in the HOMO of Table IA					
N_p	1s	2s	2px	2py	n
1s	1	-0.2219	0.	0.	2.63
2sI	0.	0.2501	0.	0.	α^c
2pxI	0.	0.	0.5777	0.	180 - 61.65
2pyI	0.	0.	0.	0.5444	
2sO	0.	1.0117	0.	0.	
2pxO	0.	0.	0.5696	0.	
2pyO	0.	0.	0.	0.6023	
coeff.	-0.0003	-0.1283	0.0988	0.1831	
hybrid:	0.5249 2s> -0.7491 2p ξ > ; coeff. in CMO: -0.2444				
N_a	1s	2s	2px	2py	n
1s	1	0.2308	0.	0.	3.29
2sI	0.	0.4054	0.	0.	α^c
2pxI	0.	0.	0.5913	0.	61.13
2pyI	0.	0.	0.	0.5861	
2sO	0.	0.8894	0.	0.	
2pxO	0.	0.	0.5571	0.5611	
2pyO	0.	0.	0.	0.	
coeff.	0.0005	0.2360	0.4360	0.7907	
hybrid:	0.2529 2s> + 0.9675 2p ξ > ; coeff. in CMO: 0.9333				

Notes. a. The system is planar, and its plane is assumed to coincide with the xy plane. b. Symbol 2s refers to the orbital obtained by contracting the original 2sI and 2sO basis orbitals and orthogonalizing to the 1s orbital according to the Schmidt procedure; symbols 2px and 2py denote the contracted p orbitals, no orthogonalization being required in this case. c. This is the angle in degrees between the resulting hybrid and the x-axis. The hybrids appear to point towards each other and practically along the H bridge.

CMO's because in them only one HMVAO would have an important weight, and of possible quasi-localized CMP's, because there only two HMVAO's would carry the highest coefficients and would be approximately directed one towards the other. In the above example, we are dealing with a situation close to a lone pair.

To further illustrate the uses of the analysis just outlined, we now briefly consider the propenimine-ammonium ion pair (I),¹⁹ the imidazole-formate ion pair (II), and the formate ion-propenimine-acrylic acid triad (III).²⁰ All three systems are characterized by the possibility of proton transfer. The most interesting questions in this case are: are there CMO's that can be interpreted as associated exclusively or mainly to the hydrogen bond? What are the local atomic polarizations in the vicinity?

It is found that, while certain MO's retain the form characteristic of the individual molecules of the pair, with very slight field effects, some have significant HMVAO coefficients only for the three bridge atoms, and can thus be classified as H-bond orbitals.

Consider in particular the changes undergone as the distance $R(N_p-H_b)$ between the propenimine nitrogen and the bridge hydrogen increases by that CMO of system (I) which corresponds to the H-bridge. When the proton is bound to N_p the MO in question is essentially the antibonding combination of the cation NH orbital and of the NH_3 lone-pair orbital; when the proton is localized at the centre of the H-bond, the same MO is essentially the anti-bonding combination of the lone pair orbitals of the two nitrogen atoms; when the bridge proton is close enough to ammonia to form the ammonium ion, then the same CMO is a linear combination of the lone-pair orbitals of N_p with the NH bonding orbital of ammonium. In the two extreme cases, the

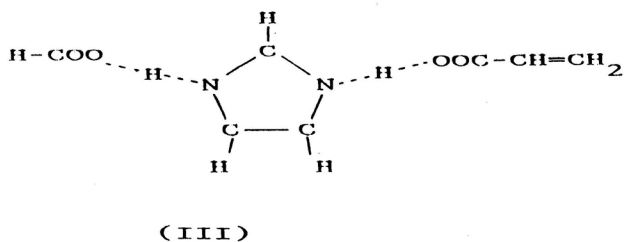
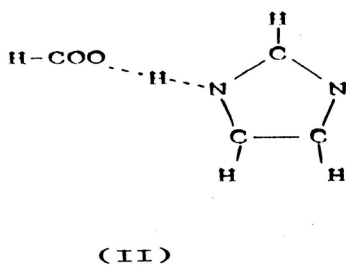
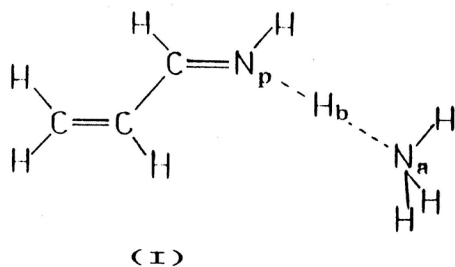


Figure 1. Molecular conformation of H-bridged systems analyzed in the MVAO scheme.

I. Propenimine-ammonium ion pair

II. Formate ion-Imidazole pair

III. Formate ion-Imidazole-Acrylic acid triad

CMO population is mainly localized on the lone pairs, while it is equally distributed on the two nitrogen atoms in the intermediate case. As to local polarizations, it turns out that, at the beginning, the propenimine nitrogen participates in the binding with an sp^2 hybrid, while the ammonia lone-pair orbitals is almost pure p (sp^8); at the end, the propenimine nitrogen is almost pure p (sp^8) and the ammonium ion is sp^2 hybridized. These results are an indication that in the CMO under consideration only the local structures of the H bond come into play. Of course, they are not related to geometrical features because, in principle, an atom participates in each CMO with a different hybrid.

The analysis of system II has revealed similar features. Interesting results have also been obtained in the analysis of system III: In the CMO's extending over the whole system the coupling between the MO's of the three fragments is conditioned by the symmetry properties of imidazole, which thus plays an active role in the transmission of effects from one side to the other of the whole system. As examples, we mention the two MO's shown in Figure 2. The first one, which has a significant involvement of imidazole, does not involve an important coupling between the two H-bridges, due to the presence of nodal planes at the two sides of the central carbon atom and to the fact that the two nitrogen AO's are not directed along the axes of the two bonds. In the other CMO, on the contrary, the AO's in question are directed along the H-bonds, and are slightly coupled to one another by the AO of the central carbon atom.

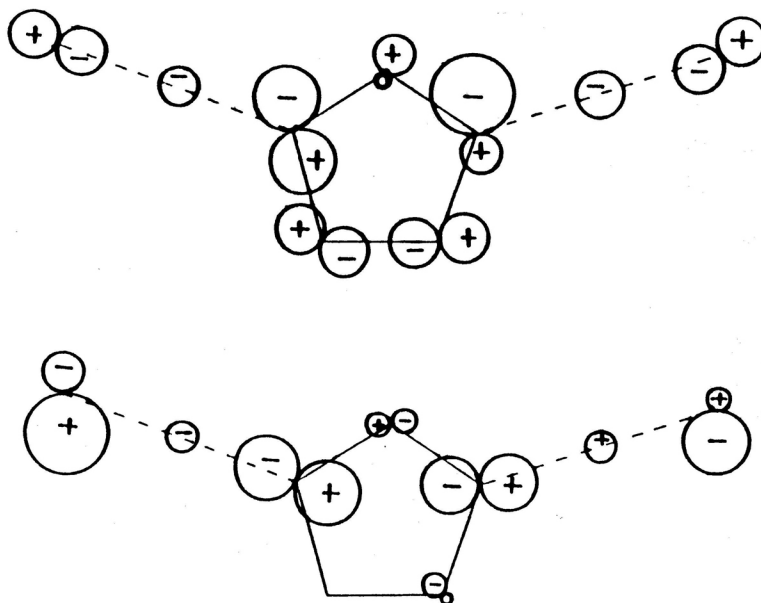


Figure 2. The main characteristic *in-situ* AOs for two selected canonical orbitals of the formate ion-imidazole-acrylic acid system. Circle radii are roughly proportional to the overall coefficient of the given AO.

As to those CMO's which have no evident localization, their expression in terms of HMVAO's is anyway useful, since it makes the correlation of the MO energies as the proton moves from one site to the other a comparatively straightforward task.

The above examples appear to support the expectation that processing of CMO's to give HMVAO's does provide a starting point for the interpretation of numerical results on CMO's in terms of such concepts as localization, polarization, *etc.* An assessment of its value would be of great interest, and it would certainly result from the study of a large number of molecules along the lines just described, for such a study would lead to the formulation of general rules.

C. A-PRIORI HYBRIDS

If quantum chemistry is to provide a theoretical framework for studies on large molecules, then it is useful to follow Pauling himself and discuss hybridization as a basis preparation prior to the computation of molecular electronic wavefunctions. We now try to briefly assess the features and merits of the *a priori* point of view in the frame of the present state of theory and computational techniques.

As it has been mentioned, in the AO theory of directed valency a σ bond between atoms A and B is identified with a doubly occupied bonding orbital formed by combining linearly one AO of A with one AO of B.

The required AO's may be pure s, p, d,...; but more generally they are hybrids obtained by combining valence AO's belonging to different angular species (*cf.* eqn A.1).

Hybridization is assumed to realize two expectations: (a), that the AO's forming the AB bond should be as strongly 'coupled' as possible with one another; (b), that they should be as weakly coupled as possible with all other AO's of the given molecule.

The word 'coupling' refers, as usual, to the matrix element of the pertinent effective one-electron Hamiltonian associated to the two AO's under consideration. The elementary theory simplifies matters by assuming that the importance of coupling is measured by overlap.²

The many successful applications of the above scheme – which may rightly be called Pauling's scheme – range from the explanation of the tetrahedral arrangement of bond in methane to the analysis of complicated multiple bonds in transition-metal complexes. Unfortunately, they are now largely overlooked, perhaps because of the lack of computer programs including hybridization as a standard feature. Even Hoffmann's highly realistic approach to the theoretical interpretation of chemical facts has curiously ignored hybridization. Yet, as already mentioned, the successes justify the efforts to put Pauling's scheme on more formal grounds within the bound orbital scheme just described.

Procedures for deriving the required hybrids for a given pure-AO basis have been briefly recalled in section 1. We focus here on our own procedure which has much in common with the others,⁴ but follows more closely the steps outlined above, and yields excellent results for the geometry of molecules such as water, ammonia and their derivatives.

Truly enough, it leaves unsolved the question of the optimal choice of the pure-AO basis;⁴ however, the success of *ab-initio* computations based on free-atom Slater orbitals – either as such or in the form of linear combinations of Gaussian orbitals – suggests that these AO's can be considered well qualified for use in the kind of study under consideration.

We will not reproduce the mathematics of our procedure but we will recall the main steps:

1. hybrids $|h'\rangle$ pointing along the bonds and overlapping as little as possible with hybrids belonging to other bonds are obtained by: (a) diagonalizing the overlap matrices associated to the various pairs of nearest neighbors of the given molecule; (b) selecting the eigenvectors corresponding to the largest diagonal element;

2. for a given atom, each hybrid $|h'\rangle$ is assigned a weight equal to the square of the pertinent overlap. The nonbonding hybrids (NBH) are taken pure *s* before orthogonalization and assigned a weight equivalent to the square of something like a standard intrabond overlap, *v.z.*, a parameter which is a measure of the tendency of NBH's to retain a high *s*-character. 0.25 is taken for doubly occupied NBH's, 0 for unoccupied NBH's [16b];

3. the set of normalized (but not orthogonal) hybrids $|h'\rangle$ of each atom is replaced by a set of new orthonormal hybrids $|h''\rangle$ by minimizing the sum of the scalar products $\langle h'|h\rangle$ weighted as above. This ensures that the new hybrids differ from the nonorthogonal ones the less the higher the pertinent intrabond overlap.

Hybrids constructed according to the procedure just outlined will be abbreviated MLHO (Maximum Localization Hybrid Orbitals). The essentials of the appropriate matrix formulation are based on the partition of the given AO basis $|\chi\rangle$, written as a row matrix, into subsets $|\chi(A)\rangle$ – where *A* denotes an individual atom – each of which is a shorter row matrix consisting of the individual AO's $|\chi(\mu,A)\rangle$ of atom *A*. This partitioning produces a corresponding partitioning of the overlap matrix $S = \langle \chi|\chi\rangle$, each block $\langle \chi(A)|\chi(B)\rangle = S(A,B)$ being the unit matrix if *A* = *B* and the original VAO's of each atom form an orthonormal set:

$$\begin{pmatrix} I & S(1,2) & S(1,3) & \dots\dots\dots & S(1,m) \\ S(2,1) & I & S(2,3) & \dots\dots\dots & S(2,m) \\ S(3,1) & S(3,2) & I & \dots\dots\dots & S(3,m) \\ \dots\dots\dots & \dots\dots\dots & \dots\dots\dots & \dots\dots\dots & \dots\dots\dots \\ S(m,1) & S(m,2) & S(m,3) & \dots\dots\dots & I \end{pmatrix} \quad (C.1)$$

where *m* is the number of atoms and *I* is the unit matrix of the order defined by the pertinent subset of $|\chi\rangle$.

Hybridization consists of a linear transformation, combining only orbitals of the same atom *A*, *i.e.* of the same subset $|\chi(A)\rangle$. Therefore, when referred to the whole basis, it is represented by a block diagonal matrix *T*, whose diagonal blocks $T(A) = \langle \phi(A)|\phi(A)\rangle$ are associated with individual atoms; *T* will be an orthogonal matrix if the basis is orthonormal. The hybridized basis $|\phi\rangle$ will then be given by the expression

$$|\phi\rangle = |\chi\rangle T, \quad |\chi\rangle = |\phi\rangle U, \quad U = T^{-1}. \quad (C.2)$$

If *T* is known, the coefficients *C*(ϕ) of the canonical orbital set $|\psi\rangle$ and the associated overlap and Flock matrices *S* and *F* can be referred to $|\phi\rangle$ by the transformations:

$$|\psi\rangle = |\chi\rangle C = |\phi\rangle U C(\chi), \quad C(\phi) = U C; \quad (C.3)$$

$$S' \equiv S(\phi) = T^+ S(\chi) T, \quad (C.4)$$

$$F' \equiv F(\phi) = T^+ F(\chi) T \quad (C.5)$$

Each new block of S' is given by

$$S'(A,B) = T^+(A) S(A,B) T(B); \quad (C.6)$$

$$F'(A,B) = T^+(A) F(A,B) T(B). \quad (C.7)$$

As a numerical example, consider the STO-3G of methane, whose geometry is shown in Figure 1. After the contraction described above, the overlap integrals of the carbon orbitals with the hydrogen orbitals are given in Table IIA.

The hybrids of Table IIA point along the axes of a tetrahedron, but do not form an orthonormal set; the procedure under consideration leads to the hybrids of Table IIB, which are the expected standard tetrahedral hybrids. According to eqns C.6 and C.7, the corresponding 4×4 blocks of S' and F' have the structure:

$$k = \begin{array}{cccc} 1 & 2 & 3 & 4 \\ \left| \begin{array}{cccc} a & b & b & b \\ b & a & b & b \\ b & b & a & b \\ b & b & b & a \end{array} \right| \end{array} \quad (C.8)$$

with $a = 0.6477$, $b = 0.1097$ for $S'(C,H_k)$,
and $a = -0.6586$, $b = -0.1516$ (au) for $F'(C,H_k)$.

The peculiarity of our method is the way in which orthogonality of the hybrids is imposed. Maximum overlap hybrids pointing along the bonds are determined for each given atom, and then the set is modified in such a way as to become orthogonal with

TABLE II
Hybridization in methane from in situ MVAO's

A. Overlap integrals between canonical ^a AO's and H atoms ^b .				
	1s(H ₁)	1s(H ₂)	1s(H ₃)	1s(H ₄)
2s	0.4884	0.4884	0.4884	0.4884
2px	0.3804	-0.3804	0.	0.
2py	0.2690	0.2690	-0.2690	-0.2690
2pz	0.	0.	0.3804	-0.3804
B. Maximum overlap and 1.p. hybrids before orthogonalization.				
2s	0.7236	0.7236	0.7236	0.7236
2px	0.5636	-0.5636	0.	0.
2py	0.3985	0.3985	-0.3985	-0.3985
2pz	0.	0.	0.5636	-0.5636
C. Components of »in situ« HMVAO's after intra-atomic orthogonalization.				
2s	0.5	0.5	0.5	0.5
2px	0.7071	-0.7071	0.	0.
2py	0.5	0.5	-0.5	-0.5
2pz	0.	0.	0.7071	-0.7071

Note a. The word »canonical« designates *in situ* MVAO's obtained by contraction and intra-atomic orthogonalization, as explained in sec. B (eqns B.1 through B.4 and Table 1B); the STO.3G level has been adopted here as in subsequent examples.

b. The columns given are distinct 4×1 blocks of the molecular overlap matrix.

as little deviation as possible from the original set. The basic idea behind this procedure can be grasped by considering the problem of constructing two orthogonal unit vectors V and W that are as close as possible to two non-orthogonal unit vectors v and w . The solution evidently lies in requiring that the angles between v and V and between w and W be as small as possible. The easiest way to formulate mathematically such a condition is to require that the sum of the two scalar products $v \cdot V$, $w \cdot W$ should be as large as possible, subject to the orthonormality conditions $V \cdot V = 1$, $V \cdot W = W \cdot V = 0$, $W \cdot W = 1$. In the simple case under consideration, the two new unit vectors V and W thus obtained form an angle of 45° with the bisectrix of the angle formed by v and w . This means that the angles between each initial vector and the final vector corresponding to it will be the same.

Symmetric solutions of the above type are found in many-dimensional cases. Unfortunately, from a physical point of view they are not completely satisfactory. In fact, suppose that v and w actually represent two hybrids, v forming a strong bond, w a weak one. Then, it would be more reasonable to orthogonalize the two vectors in such a way that V should be much closer to v than W to w . This suggestion is based on the following physical argument. Localization requires intra-atomic orthogonality of the AO's representing atoms in the molecule, because otherwise they would be strongly coupled *via* intra-atomic matrix elements (over and beyond the unexpressible electrostatic interaction of occupied orbitals), and electrons would easily pass from one to the other. This gives rise to a sort of repulsion tending to displace the bonding AO's of a given atom from the direction of the bonds to which they belong until they become orthogonal to one another. However, hybrids more strongly involved in bonds will oppose the repulsion more effectively than weakly binding ones, and, therefore, the process will take place in such a way that hybrids less involved in their bonds will be most easily displaced. If applied in the context of a maximum overlap procedure, this physical interpretation uses overlap as a measure of »bond energy«, but it should be remembered that energy is the physical quantity actually under consideration. The explicit recognition of this point will be particularly useful in the treatment of 'secondary' hybridization, *viz.* the hybridization of lone pairs.

Thus, if the orthogonalization procedure must match physical requirements, the strengths of the bonds formed by the individual hybrids of each given atom must be taken into account. This can be done in a straightforward manner by multiplying each scalar product by a weight factor related to the corresponding overlap so that the maximization procedure mentioned above will bear on a weighted sum of scalar products where the 'weaker' hybrid will count less than the stronger one. The question remains what to do with nonbonding hybrids. The following argument suggests a reasonable solution. Since the s AO of the isolated atom has a lower energy than the associated p , d , ... orbitals, electrons not shared with another atom would tend to occupy a pure- s orbital if there were no orthogonality constraint. Thus, a nonbonding hybrid before orthogonalization must be assigned a pure- s form. Its weight cannot be zero, because, as it has been mentioned, there is a competition between the different hybrids, and if the weight were zero, the nonbonding hybrid would have to adjust to the others regardless of the energy expense involved. It has been suggested that a fictitious bond could be introduced by placing, say, a hydrogenoid atom at a suitable distance, but no clearcut criterion for choosing the position and the AO characteristics of the fictitious atom are available; moreover, it must be expected that the nonbonding hybrid will be more or less adaptable, depending on its population. As already mentioned, an empiri-

TABLE III
Hybridization in the Ammonia Molecule

A. Overlap integrals between canonical ^a AO's and H atoms.				
	1	2	3	
2s	0.5004	0.5004	0.5004	
2px	0.4114	-0.2057	-0.2057	
2py	0.	0.3562	-0.3562	
2pz	0.1637	0.1637	0.1637	
B. Maximum overlap and 1.p. hybrids before orthogonalization.				
2s	0.7490	0.7490	0.7490	1.
2px	0.6157	-0.3078	-0.3078	0.
2py	0.	0.5332	-0.5332	0.
2pz	0.2450	0.2450	0.2450	0.
C. Overlap values λ				
	0.6682	0.6682	0.6682	0.25 ^b
D. Orthogonalized hybrids h1, h2, h3, 1p				
2s	0.4599	0.4599	0.4599	0.6945
2px	0.8165	-0.4082	-0.4082	0.
2py	0.	0.7071	-0.7071	0.
2pz	0.3490	0.3490	0.3490	-0.7966
E. Overlap values on the new hybrids				
h1	0.6232	0.1194	0.1194	
h2	0.1194	0.6232	0.1194	
h3	0.1194	0.1194	0.6232	
1p	0.1721	0.1721	0.1721	
F. Fock-matrix elements over the new hybrids (au)				
h1	-0.7495	-0.2081	-0.2081	
h2	-0.2081	-0.7495	-0.2081	
h3	-0.2081	-0.2081	-0.7495	
1p	-0.2357	-0.2357	-0.2357	

^a Seenote a, Table II. ^b Value assigned to the doubly occupied non bonding hybrid.

cal adjustment leads to the conclusion that the weight to be given to a doubly occupied nonbonding hybrid corresponds to a pseudo-overlap of 0.5 regardless of the atom to which it belongs.^{16c} The kind of numerical results obtained is illustrated in Table III.

D. DISCUSSION: HYBRIDS, LOCALIZATION, STRAIGHT BONDS

The procedure outlined in the preceding section is »a priori« inasmuch as it is independent of previous computations, but here it has been used in combination with the results of sec. B, as an »external« procedure in the sense of Daudel *et al.*,⁹ namely one introducing an independent criterion for the processing of the output of *ab initio* MO computations. The steps illustrated so far consist of the construction from canonical orbitals of a minimal basis of *in situ* modified AO's, of the determination of their overlap matrix from the initial overlap matrix (eqns B.1 through B.6), and of the appli-

cation of our maximum localization procedure in order to obtain a final basis involving, in addition to the inner shells, *in situ* HMVAO's-hybridized modified valence atomic orbitals. These have been used on the examples of methane and ammonia to compute the overlap matrix and the matrix representing the Fock operator on the final HMVAO basis. We now proceed to a more detailed discussion of the matrices in question for the simple cases just mentioned, and present the extension of the method used to molecules including additional special features, like π -electron systems and strained bonds. We, thus, come to the question of directed valency.

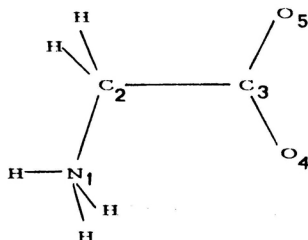
First of all, let us consider methane and ammonia. The main question is: how good is the localization obtained by the hybrids according to our procedure? The answer, of course, depends on the criterion used for localization. We stick here to the simplest one, namely the existence of a reasonable representation of the molecule in terms of two-AO two-centre molecular orbitals. This changes the question into the following: is it reasonable to neglect overlap values of 0.11 *vs.* 0.65 (eqn C.8) or even 0.17 *vs.* 0.62 (Table IIIe)? Is it reasonable to neglect Fock-matrix elements of -0.15 *vs.* -0.66 (eqn C.8), or -0.24 *vs.* -0.75 (Table IIIf)?

Two kinds of arguments, giving apparently opposing answers, can be invoked here. There is a physical argument which stands in favour of a positive answer: the smaller elements reported above fall within the range of the order of magnitude of inter-bond matrix elements found by any localization method, and therefore, since localization is a fact proven by chemistry independently of quantum mechanics, they *must be* reasonable. The real problem is how to explain why such smaller elements should correspond to the so-called »non-bonding interactions«, whereas the larger ones correspond to bonds.

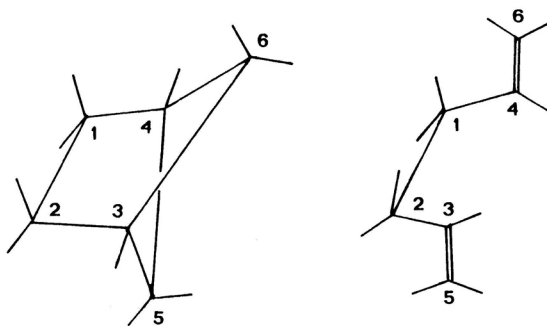
There is also a mathematical argument. Neglect of the smaller values gives rise to an orbital description of the molecular system which can be considered as a first order approximation to the complete SCF treatment. Now, according to perturbation theory, it is not the neglected elements that measure the quality of the approximation, but their squares divided by the differences of the pertinent diagonal elements of the partially diagonalized matrix, unless the diagonal elements in question are equal. Unfortunately, this second argument does not bring anything new, because the application to the methane Fock matrix over hybrids of a transformation T which diagonalizes the blocks corresponding to the CH bonds yields couplings of -0.21 au between degenerate pairs of bonding orbital energies (all equal to -0.6650 au), and -0.11 between pairs of antibonding orbital energies (all equal to 0.6357).

Clearly, the matter must be further analyzed, but a way out of the apparently conflicting results is the consideration that coupling elements are large even between an inner shell orbital of one atom and a valence shell orbital of another. This is the result of two-electron interactions (especially the Coulombic ones), and will cancel with nuclear repulsion terms as well as with those two-electron terms which appear in the total energy expression in addition to orbital energies. We will discuss this point in subsequent papers.

In connection with matrix elements, it may be useful to remind the reader that the applicability of empirical rules connecting Fock-matrix elements to overlap (*e.g.* the Wolfsberg-Helmholtz rule,²⁴ Cusachs's rule,²⁵ *etc.*) is also a point for further study, because these rules are not invariant under linear transformations. Updating of a critical analysis made by our group a long time ago²⁶ might be illuminating.



(a)



(b)

(c)

Figure 3. Molecular conformations of α -glycine zwitterion (a), bicyclo[2,1,1]hexane (b) and (c). The latter is essentially 1,5-hexadiene and is obtained as intermediate step in the isomerization of (b).

Before leaving the simplest molecules, a very interesting result, deserving reflection, is that in ammonia our hybrids produce an energy of -0.4761 au for the lone-pair orbital, which is very close to the energies of the other hybrids (-0.5057 au), whereas the canonical orbital corresponding to the lone pair has an energy of -0.3521 au. This is an indication that our choice of the lone-pair »weight« has some deeper foundation than mere empiricism.

We now come to two less speculative questions: how does hybridization perform in the case of π bonds and in the case of strained bonds? We have chosen as concrete examples the α -glycine zwitterion (Figure 3a) for the former point, and bicyclo (2,1,1) hexane (Figures 3b,c) for the latter.

Table IV contains information concerning the atoms of the carboxyl anion C_3 and O_4 (the other oxygen is equivalent to O_4).

TABLE IV

Results for the COO^- group of the α -glycine zwitterion referred to a hybridized basis

A. Hybrids of carbon and oxygen ^a .								
	C_3				O_4			
2s	0.5822	0.5749	0.5749	0.	0.4968	0.6137	0.6137	0.
2px	0.	0.7071	-0.7071	0.	-0.7705	0.6373	-0.0135	0.
2py	-0.8131	0.4117	0.4117	0.	-0.3994	-0.4661	0.7894	0.
2pz	0.	0.	0.	1.	0.	0.	0.	1.
B. Fock-matrix atomic blocks in triangular form.								
h1	-0.482	-0.164	-0.157	0.	-0.559	-0.305	-0.295	0.
h2		-0.681	-0.081	0.		-0.464	-0.249	0.
h3			-0.677	0.			-0.428	0.
h4				-0.074				-0.084
C. Overlap and Fock-matrix blocks $\text{C}_3\text{-O}_4$.								
h1	0.073	0.103	-0.092	0.	-0.156	-0.138	-0.104	0.
h2	0.639	0.174	0.186	0.	-0.898	-0.303	-0.299	0.
h3	0.040	-0.098	0.088	0.	-0.092	-0.113	-0.110	0.
p	0.	0.	0.	0.191	0.	0.	0.	-0.284

Note a. The σ hybrids of carbon are sp^2 within 3% and point almost exactly along the bonds, as does the σ bonding orbital of oxygen. The lone pair orbitals of oxygen are $sp^{1.66}$ hybrids forming an angle of 127° , while the σ bonding hybrid is practical tetrahedral, with $n = 3.05$.

Table IV requires little comment, for it just illustrates a point confirmed by our experience on a large number of cases, namely that π bonds are treated correctly in our scheme, and that a molecule more complicated than ammonia or methane does not present any special difficulty, even as regards lone pairs.

The results on the hydrocarbon of Figure 3b are shown in Table V.

Table Vb shows that the CC bonds are all more or less »bent«, for the hybrids do not point along them. This is a situation typical of small cycles,²⁷ and is in agreement with Bayer's classical theory. Experimental evidence shows that these cycles are metastable: under sufficient perturbation they tend to rearrange to a situation where the bonds are »straight«. This consideration has in fact suggested a method for following the evolution of a reaction, which consists of computing the *orthogonalized* maximum-overlap hybrids for an initial configuration of the reacting molecules, displacing the atoms towards the geometry that would make the bonds straight with the given hybrids, computing the hybrids for the new situation, and so on. The procedure converges, and yields, for example, a reasonable reaction path for the addition of H_2 to CO absorbed on iron to form the secondary alcohol structure FeCHOH , which explains the formation of methanol as a by-product of the Fischer-Tropsch reaction.²⁸ We cannot dwell here on this application but we make some comments on directed valency and straight bonds using bicyclo[2,1,1]hexane as an example.

As long as D_2 symmetry is imposed, the two triangular »ears« of bicyclo[2,1,1]hexane (Figure 3b) are predicted by geometry optimization.

When, however, the two atoms, C_3 and C_6 are somewhat shifted by raising the 2-3 bond and lowering the 1-4 bond above and below the 1,2,3,4 plane, respectively, optimization of the geometry yields the open conformation of Figure 3c. Hybridization

TABLE V

Hybridization from an STO-3G computation in bicyclo[2,1,1]hexane (D₂ symmetry)

A. Initial geometrical parameters (angstroms and degrees).					
Distances			Angles		
C ₁ C ₂	1.558		C ₁ C ₂ C ₃	99.5	
C ₂ C ₃	1.545		C ₂ C ₃ C ₅	100.8	
C ₃ C ₅	1.564		C ₅ C ₃ C ₆	86.8	
C ₄ C ₅	1.564		C ₃ C ₅ C ₄	82.6	
C ₃ H ₇	1.095		H ₁₃ C ₅ H ₁₄	108.0	
C ₅ H ₁₃	1.099		H ₉ C ₂ C ₃	112.4	
B. Characteristics of hybrid orbitals.					
Atom	Hybrid	<i>n</i>	deviation (deg)		
C ₁	h1	3.40	C1C ₂	4.0	
	h2	3.35	C ₁ C ₄	3.7	
	h3	2.68	C ₁ H ₁₁	2.6	
	h4	2.68	C ₁ H ₁₂	2.6	
C ₃	h1	3.23	C3C ₂	5.6	
	h2	3.80	C ₃ C ₅	10.5	
	h3	3.80	C ₃ C ₆	10.5	
	h4	1.89	C ₃ H ₈	0.9	
C ₅	h1	3.75	C5C ₃	11.3	
	h2	3.75	C ₅ C ₄	11.3	
	h3	2.41	C ₅ H ₁₃	3.4	
	h4	2.51	C ₅ H ₁₄	2.7	
C. Overlap values					
C-C bonds: from 0.564 to 0.592					
C-H bonds: from 0.648 to 0.648					
interbond: 0.12 to 0.15					

processing yields the straight bonds and higher overlaps reported in Table VI. In our opinion, this is an excellent indication of the validity of arguments based on hybridization for predicting molecular geometries. The increase of bond overlaps also show that the combination of maximum overlap criteria with the »straight bond« condition referred to orthogonal hybrids may represent the actual features of molecular reality.

E. CONCLUSION

The moral of section D is that certain features of molecules discovered on purely intuitive grounds by the pioneers of quantum chemistry, in particular by Linus Pauling, prove to be rooted in molecular reality even when seen in the light of computational progress. This holds in particular for hybridization. Of course, much remains to be done if this concept is to be fully recovered and used in combination with sophisticated computations as a tool for the coming developments of theoretical chemistry. We have pointed above to some of the open problems, which range from a less intuitive justification of AO orthogonality to a better definition of the »straight bond« concept. In our opinion, it is high time for these problems and others of the same sort to resume the central place on the stage of quantum chemical research, because experiments are getting more and more involved with large molecules and atom clusters,

TABLE VI

Hybridization from an STO-3G computation in bicyclo[2,1,1]hexane (distorted)

A. Initial geometrical parameters (angstroms and degrees) ^a .				
Distances		Angles		
C ₁ C ₂	1.538	C ₁ C ₂ C ₃	113.8	
C ₂ C ₃	1.495	C ₂ C ₃ C ₅	123.8	
C ₃ C ₅	1.328	C ₂ C ₃ H ₇	115.6	
C ₄ H ₇	4.015	C ₃ C ₅ H ₁₃	122.9	
C ₃ H ₇	1.098			
C ₅ H ₁₃	1.084			
B. Characteristics of hybrid orbitals.				
Atom	Hybrid	<i>n</i>	deviation (deg)	
C ₁	h1	3.12	C ₁ C ₂	2.0
	h2	2.87	C ₁ C ₄	2.3
	h3	2.93	C ₁ H ₁₁	1.6
	h4	3.09	C ₁ H ₁₂	2.0
C ₃	h1	2.26	C ₃ C ₂	1.0
	h2	1.60	C ₃ C ₅	0.6
	h3	∞	C ₃ C ₆	90.0
	h4	2.25	C ₃ H ₈	1.8
C ₅	h1	1.62	C ₅ C ₃	0.
	h2	∞	C ₅ C ₄	90.0
	h3	2.23	C ₅ H ₁₃	1.3
	h4	2.23	C ₅ H ₁₄	1.3
C. Overlap values				
C–C bonds: from 0.754 to 0.601				
C–H bonds: from 0.663 to 0.642				
interbond: 0.12 to 0.15				

which interest experimentalists not just as static isolated systems, but as participants in complicated reactions. Vibrational states, reaction paths with their potential energy profiles and time evolution should be predicted at least qualitatively. Now, even granting that science should be reduced to highly sophisticated black-box computations, it seems obvious that a brute-force approach is either not feasible or not usable for the electronic states of such systems as, say, haemoglobin, for one thing because of the size of the output. We must be able to process these or simpler computations so as to arrive at general rules enabling us to focus reflection as well as further computational efforts on the points essential for each given problem. Now, rules for processing, explaining and predicting is one of the key concepts. We hope we have convinced the reader that, after all, Pauling's concept of hybridization is one of the key concepts and should be more effectively used in computational chemistry, as well as in interpretational theoretical studies.

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SAŽETAK

Paulingova hibridizacija kao oruđe komputacijske kemije

G. Del Re i F. Zuccarello

Uloga Paulingova modela hibridizacije atomskih orbitala u interpretativnoj kvantnoj kemiji potanko je razmotrena s povijesnog gledišta, s posebnim osvrtom na doprinos prvog autora tom području. Osobito je istaknuta potreba interpretacije vrlo složenih molekulskih valnih funkcija s pomoću hibrida.