HYBRIDIZATION BY THE MAXIMUM OVERLAP METHOD

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Contents

I. Introduction 43
II. Application of Overlap Integrals for Discussing Bonding 45
  A. Outline of the Method 45
  B. Worked Example 46
III. Application of the Maximum Overlap Method to Hydrocarbons 47
  A. Calculated Hybrids, Bond Overlaps, and Deviation Angles 47
  B. Correlations between the Hybridization Obtained by the Maximum Overlap Method and Experimental Quantities 50
  C. Comparison of Maximum Overlap Hybridization with Results of Other Semiempirical Methods 51
IV. Application of the Maximum Overlap Criterion to Molecules with Several Different Atoms 52
V. Concluding Remarks 53

I. Introduction

One of the aims of theoretical chemistry has been to develop useful models for describing molecular systems. Ever since the formulation of the fundamental laws of the quantum theory by Heisenberg in 1925 and Schrödinger in 1926, and the first application of the quantum mechanics to a molecular system—H_2 molecule—by Heitler and London in 1927, it became clear that the ultimate description of molecular systems has to be based on the new quantum concepts. However, the molecules of interest in chemistry are too complex to be treated in full exactness, and, on the other hand, even if the exact wavefunctions are available, the mere tabulation of the overall electron distribution of a complex molecule is not what would interest most chemists. Chemistry has developed its own concepts and models, and what is wanted is a new interpretation of these. One should try to attribute a deeper meaning to the existing models, as well as to make necessary modifications and revisions of established concepts in developing more adequate models for describing molecules.

The problems in chemistry which have been studied by the methods of quantum mechanics may conveniently be grouped into those which are treated by exact methods and maximal accuracy as one extreme, and those which are empirical in part, sometimes even without a full theoretical background, but nevertheless useful in helping chemists to systemize and rationalize the enormous wealth of experimental data. With the present availability of computers, the differentiation between the two approaches is becoming more evident; but it is also becoming clearer that the two approaches serve different purposes, are frequently concerned with different problems, and use different concepts, and their results are of different kinds. It is also clear that nonempirical calculations will not displace and finally eliminate the simple semiempirical methods. The most that one expects, and what is desirable in the future expansion of *ab initio* calculations on larger and more complex systems, is to obtain a fuller justification and clear indication of the limitations of various semiempirical methods and the concepts used for description of bonding in molecules.

In this review we are concerned with one of the important concepts in chemistry, that of hybridization. In particular, we will consider some more recent developments and application of generalized hybrids for description of molecules. As is well known, Linus Pauling, in order to resolve the difficulty of accounting for directional properties of chemical bonds, introduced the concept of atomic orbital hybridization. The free atom orbitals s, p_x, p_y, p_z, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}, and d_{z^2} when used for an approximate description of electrons in a molecule cannot account for the characteristic valence angles, such as the angles of 180°, 120°, and 109° 28′ (tetrahedral) found in various carbon compounds. However, the above *nine* atomic orbitals have to account for the geometrical forms of most molecules if we accept the plausible assumption that atoms retain to a considerable extent their individuality after forming a molecule. Moreover, if we limit ourselves to the chemistry of carbon atom and other first-row elements, the first *four* orbitals have to account for almost *all* the diversity of molecular shapes met in organic chemistry. Any model which intends to be finally related to the basic principles (Schrödinger equation) has to be based then on the above set of atomic orbitals. To derive the valence angles of 180°, 120°, and 109° 28′, Pauling introduced particular linear combinations of the initial free-atom orbitals. To construct three equivalent orbitals in a plane, for example, we select s, p_x, and p_y orbitals and consider their linear combinations.

$$\begin{aligned}\psi_1 &= a_1(\mathrm{s}) + b_1(\mathrm{p}_x) + c_1(\mathrm{p}_y)\\ \psi_2 &= a_2(\mathrm{s}) + b_2(\mathrm{p}_x) + c_2(\mathrm{p}_y)\\ \psi_3 &= a_3(\mathrm{s}) + b_3(\mathrm{p}_x) + c_3(\mathrm{p}_y)\end{aligned} \tag{1}$$

Since we require three *equivalent* orbitals, *i.e.*, orbitals of the same s–p composition, which then insures that the orbitals are of the same shape but differ only in their orientation in the space, it immediately follows that $a_1 = a_2 = a_3 = {}^1/_3{}^{1/2}$. If the hybrid ψ_1 is directed along the x axis, $c_1 = 0$ since the p_y orbital cannot contribute to build charge along the x axis, being of wrong symmetry. Thus

$$\psi_1 = \sqrt{\frac{1}{3}}(\mathrm{s}) + \sqrt{\frac{2}{3}}(\mathrm{p}_x) \tag{2}$$

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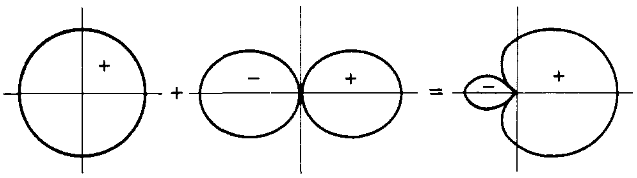

Figure 1. A superposition of an s and p orbital producing an sp hybrid.

The coefficients a_1 and b_1 are constrained by the orthogonality condition, $a_1^2 + b_1^2 = 1$, which scales the overall size of the orbital to correspond to a single electron. The hybrids ψ_2 and ψ_3 share the p_y orbital and the remaining part of the p_x equally, giving

$$\begin{aligned}\psi_2 &= \frac{1}{\sqrt{3}}(\mathrm{s}) - \frac{1}{\sqrt{6}}(\mathrm{p}_x) + \frac{1}{\sqrt{2}}(\mathrm{p}_y)\\ \psi_3 &= \frac{1}{\sqrt{3}}(\mathrm{s}) - \frac{1}{\sqrt{6}}(\mathrm{p}_x) - \frac{1}{\sqrt{2}}(\mathrm{p}_y)\end{aligned} \tag{3}$$

ψ_1, ψ_2, and ψ_3 are the so-called trigonal hybrids, designated as sp^2. So constructed hybrids not only have the desired directional properties but also are more efficient in overlapping with another orbital than the original atomic orbitals s, p_x, and p_y, as their lobes are better shaped for penetrating toward another atom (Figure 1).

Equivalent hybrids, characterized by an equal amount of s–p–d contributions, have played an important role in development of quantum chemistry. However, the experimental evidence accumulated in recent years reveals some details, a smaller variation of various molecular properties, which cannot be explained by describing the bonds of relevant atoms with equivalent hybrids. For example, the variations of single C–C bond lengths are well established, indicating the asymmetry of the immediate environment of particular carbon atoms. A description of such nonequivalent bonds necessitates a revision of the initial concept on hybrids and removal of the restriction that all hybrids of a particular set should have the same s–p–d content. If, for example, only two of the three bonds in a planar trigonal configuration are equivalent, the situation will be described by

$$\begin{aligned}\psi_1 &= a(\mathrm{s}) + b(\mathrm{p}_x)\\ \psi_{2,3} &= [(1 - a^2)/2]^{1/2}(\mathrm{s}) - [(1 - b^2)/2]^{1/2}(\mathrm{p}_x) \pm {}^1/_2{}^{1/2}(\mathrm{p}_y)\end{aligned} \tag{4}$$

Here a may take any value between 0 and 1. An application of these more general hybrids, which may be designated as sp^n, where n is not restricted to be 1, 2, and 3, but may be a fractional number, leads to the problem of how to determine the best set of the coefficients a_i, b_i. In this review we are, in particular, concerned with the problem of construction of hybrid orbitals, *i.e.*, of determining the coefficients a_i, b_i, by adopting the criterion, sometimes called principle, of maximal overlapping. How useful these hybrids are, how well they can account for the diversity of bonds and various molecular properties, what experimental quantities can be correlated with the computed hybrid parameters, and finally what are the limitations of the model based on the generalized hybrids are the subject of the main part of this review.

After Pauling's initial work,[1] Hultgren considered hybrids of more general form,[2] while Van Vleck discussed the idea of equivalent localized bonds and worked back to the atomic orbitals and hence to hybrids.[3] In 1940, Kimball examined hybrids for various geometries applying group theoretical methods and showed that in most cases there is more than one possible hybrid composition.[4] For example, in square-planar structures, we have besides Pauling's dsp^2 also d^2p^2 hybrids as an alternative. Energetically, the two possibilities are not equivalent. A general linear combination, $\phi = c_1(dsp^2) + c_2(d^2p^2)$, in which the coefficients c_1 and c_2 have to be determined for individual cases, presents the final answer.

Since the actual calculation of the total energy is not practical for most but the simplest molecules, an approximate method has be be adopted. The criterion of maximum overlapping, originally due to Pauling and Slater,[5] appears very attractive for determination of the relative weights of various possibilities at this level of sophistication. It is based on intuition and has no firm theoretical basis. It can be justified, however, as follows. The dominant contribution to the binding energy of molecules come from contributions which have no classical analogy. The magnitude of these contributions arises from those regions in space in which the product $\phi_a\phi_b$, where ϕ_a and ϕ_b are atomic orbitals centered on different nuclei, is relatively not a small quantity. In other words, the larger the region with $\phi_a\phi_b$ not being small, the magnitude of which can be measured by the overlap integral $S = \int\phi_a\phi_b d\tau$, one expects the resulting bonds to be stronger. An application of such a qualitative criterion requires some caution, because in some cases other factors are of importance. For example, the overlapping orbitals have to be of approximately the same energy.[6] In the early discussions of bonding, Pauling assumed that the hybrid amplitude, *i.e.*, the maximal magnitude of the angular part of the hybrid orbital, is a measure of the strength of a hybrid—he did not say much about the overlap integral. He showed that the bond energy varies closely as the [strength of hybrid 1]$^{1/2}$[strength of hybrid 2]$^{1/2}$. However, in order to define the strength, he had to assume that all radial functions of the atomic orbitals to be mixed together were the same. This is a liability from which the maximum overlap criterion does not suffer. Hence, all the early application of the principle of maximum overlap was devoid of an actual overlap calculation and the arguments resulted on maximizing the angular amplitude of an orbital.[7] Maccoll[8] reinvestigated Pauling's conditions and has given a slightly changed formulation. In some cases, however, other factors besides overlapping may be important. Fischer (-Hjalmars)[9] considers the role of the kinetic and the potential energy of electrons in effectively screened fields of the nuclei yielding a "condition of maximum penetration." Similarly, for qualitative discussions of the effects that determine the size and the shapes of orbitals, Stewart and Eyring introduced "principle of minimum bend-

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(1) L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, 14, 359 (1928); *J. Amer. Chem. Soc.*, 53, 1367 (1931).

(2) R. Hultgren, *Phys. Rev.*, 40, 891 (1932).

(3) J. H. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, 7, 167 (1935).

(4) G. E. Kimball, *J. Chem. Phys.*, 8, 188 (1940).

(5) L. Pauling, *J. Amer. Chem. Soc.*, 53, 3225 (1931); J. C. Slater, *Phys. Rev.*, 37, 481 (1931); 38, 1109 (1931); R. S. Mulliken, *ibid.*, 41, 67 (1932).

(6) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, Oxford, 1952, p 104 ff; *Proc. Phys. Soc., London*, 33, 111 (1937).

(7) H. Kuhn, *J. Chem. Phys.*, 16, 727 (1948); G. H. Duffey, *ibid.*, 17, 196, 1328 (1940); 18, 128, 510, 943, 746, 1444 (1950).

(8) A. Maccoll, *Trans. Faraday Soc.*, 46, 369 (1950).

(9) I. Fischer, *Ark. Fys.*, 5, 349 (1952); I. Fischer-Hjalmars, *ibid.*, 7, 165 (1953).

(10) G. H. Stewart and H. Eyring, *J. Chem. Educ.*, 35, 550 (1958).

ing of orbitals,"[10] which is based on considering the kinetic energy of electrons.

A revival of interest in the problem of construction of hybrids was initiated by the work of Murrell.[11] He developed a method for the construction of hybrids for the XY_n system using the criterion of maximum overlapping. Murrell constructed an overlap matrix R between the orbitals of the central atom and the ligand orbitals. The method is suitable for application to systems with little or no symmetry, *i.e.*, systems with nonequivalent bonds. Gołebiewski[12] has shown that the approach of Murrell is equivalent to diagonalization of product $R\tilde{R}$, which considerably simplifies the computations. Lykos and Schmeising[13] have shown that the overlap matrix R is only a part of a complete overlap matrix of the molecule which involves also ligand–ligand overlaps neglected by Murrell, and which can be associated with an eigenvalue problem: $SC = C\Lambda$, if S, the overall overlap matrix, is nonsingular (*i.e.*, $\det(S) \neq 0$). The significance of the results of Lykos and Schmeising is that now the problem of hybrid construction is converted into an eigenvalue problem, and direct comparisons with semiempirical calculations are possible. They have even shown that for systems with all bonds equivalent the well-known Hückel method is identical with maximum overlap calculations. The two methods differ when nonequivalent bonds are present, but even in such cases the difference may be considerably reduced if appropriate weighing is introduced in the overlap matrix.

II. Application of Overlap Integrals for Discussing Bonding

The early application of overlap integrals to discussion of bonds indicated the correct relative strength of various C–H bonds,[14] while the previous conclusions based on hybrid amplitudes lead to a reverse order. As we go from sp^3 to sp^2 and sp, the evaluated bond overlap and the experimental bond energy increases. This initial success encouraged discussion of bonding in terms of overlaps, for example, the discussion of the relative strength of equatorial and axial bonds[15] in PF_5. An application of overlap integrals to construction of hybrids in quadricovalent XY_4 systems indicated the importance of taking into consideration ligand orbitals, which simple approaches based on hybrid amplitudes ignore.[16]

In the above-mentioned calculations, Slater orbitals[17] were assumed when evaluating the overlap integrals. Available tables of overlap integrals for the most important combinations of Slater-type orbitals[15,18] facilitated applications. It became evident, however, that Slater orbitals are deficient in some details and that it may be of some advantage to use better wavefunctions. In the application of the maximum overlap method to highly strained systems, contributions from π-type overlap arise, which are somewhat underestimated for Slater orbitals.[19] Slater functions are particularly bad for d orbitals, whose size varies greatly with ionic character. Of several alternative sets of orbitals available, we will only mention those of Burns[20] and Clementi.[21] Burns suggested revised screening constants for Slater orbitals, selected to produce better overlap integrals when compared to the corresponding integrals based on Hartree–Fock orbitals. Clementi supplied functions of the so-called double-zeta type, first considered by Richardson.[22] They are orthogonal, specified by several parameters, and are more flexible to adjust to resemble more elaborated SCF wavefunctions. Tables of basic overlap integrals for Clementi orbitals for the most important region of internuclear separations are available.[23]

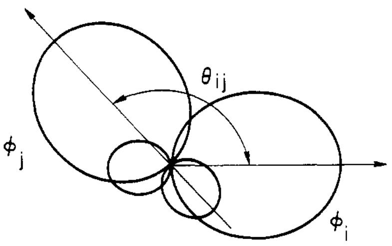

Figure 2. Interorbital (interhybrid) angle θ_{ij}.

A. OUTLINE OF THE METHOD

The well-known sp, sp^2, and sp^3 hybrids form a special case of hybridization when two, three, or four equivalent bonds to an atom are formed. Their s–p composition follows from the symmetry requirements. In a general case, hybrids are of the form: $\phi_i = a_i(s) + b_i(p_i)$, where (s) and ($p_i$) stand for a carbon 2s and 2p orbital of a particular orientation. Here all a_i and b_i need not be the same, thus giving nonequivalent hybrids. The coefficients have to satisfy the orthogonality conditions:[24] $a_ia_j + b_ib_j \cos \theta_{ij} = 0$ for $i \neq j$, and equal 1 for $i = j$ (Figure 2). θ_{ij} is the angle between the directions of hybrids ϕ_i and ϕ_j, which is determined by the relative orientation of their respective p orbitals. We see from the orthogonality conditions that the larger the p character of the hybrids (larger b/a values), the smaller will be the valence angle θ_{ij}, which tends to 90° when the orbitals are pure p. An orbital $\phi = a(s) + b(p)$ may be represented as s^mp^n, where m, n correspond to the coefficients a, b by the relationship $a^2:b^2 = m:n$. We can thus speak of the fraction $m/(m + n)$ of s character, and a fraction $n/(n + m)$ of p character. Usually, however, we choose $m = 1$ and write hybrids as sp^n.

In the method of maximum overlap, we search for the optimal parameters a_i, b_i for all hybrids of all atoms in a

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(11) J. N. Murrell, *J. Chem. Phys.*, 32, 767 (1960).

(12) A. Gołebiewski, *Trans. Faraday Soc.*, **57**, 1849 (1961).

(13) P. G. Lykos and H. N. Schmeising, *J. Chem. Phys.*, **35**, 288 (1961).

(14) R. S. Mulliken, *J. Amer. Chem. Soc.*, 72, 4493 (1950).

(15) F. A. Cotton, *J. Chem. Phys.*, **35**, 228 (1961). However, see also R. G. A. R. Maclagan, *J. Chem. Soc. A*, 2992 (1971), who discusses the importance of the use of contracted 3d orbitals, and demonstrates that the overlap criterion should be used with caution in connection with 3d orbitals.

(16) M. Randić, *J. Chem. Phys.*, **36**, 3278 (1962); *Croat. Chem. Acta*, **34**, 231 (1962).

(17) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(18) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949); H. H. Jaffé and G. O. Doak, *ibid.*, **21**, 196 (1953); H. H. Jaffé, *ibid.*, 21, 258 (1953); D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 354 (1954); D. A. Brown and N. J. Fitzpatrick, *J. Chem. Phys.*, **46**, 2005 (1967); L. Leifer, F. A. Cotton, and J. R. Leto, *ibid.*, **28**, 1253 (1958).

(19) L. Klasinc, Z. Maksić, and M. Randić, *J. Chem. Soc.*, 755 (1966). Cyclopropane, cyclobutane, and cubane have also been considered by A. Veillard and G. Del Re, *Theor. Chim. Acta*, 2, 55 (1964), who adopted a general procedure derived by G. Del Re, *ibid.*, **1**, 197 (1963).

(20) G. Burns, *J. Chem. Phys.*, **41**, 1521 (1964).

(21) E. Clementi, "Tables of Atomic Functions," a supplemennt to *IBM. J. Res. Develop.*, **9**, 2 (1965).

(22) J. W. Richardson, *J. Chem. Phys.*, **35**, 1829 (1961).

(23) L. Klasinc, D. Schulte-Frohlinde, and M. Randić, *Theor. Chim Acta*, **8**, 358 (1967); *Croat. Chem. Acta*, **39**, 125 (1967); **41**, 51 (1969).

(24) N. F. Mott and I. N. Sneddon, "Wave Mechanics," Dover Publications, New York, N. Y., 1963.

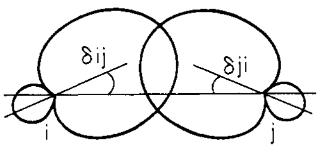

Figure 3. Angles δ_{ij} and δ_{ji} measuring the amounts of deviations of hybrid directions from a straight line joining two atoms.

molecule which will maximize the sum over all bonds of suitably scaled bond overlaps.

$$S_{\text{total}} = k_{\text{CC}}\Sigma S_{\text{CC}} + k_{\text{CH}}\Sigma S_{\text{CH}} \qquad (5)$$

Here S_{CC} and S_{CH} are bond overlaps for CC and CH bonds. Generally, the directions of hybrids and the line joining two carbon atoms may diverge (Figure 3) and S_{CC} is calculated by decomposition into contributions arising from σ and π overlap.[19] Factors $k_{\text{CC}} = 121$ and $k_{\text{CH}} = 136$ are selected so that they produce CC and CH bond energies in kcal/mol in ethane, assuming the proportionality $E_{\text{CC}} = k_{\text{CC}}S_{\text{CC}}$ and $E_{\text{CH}} = k_{\text{CH}}S_{\text{CH}}$. Details of the method may be found in ref 19, 25, and subsequent work. The hybrids for various hydrocarbons discussed here are calculated using Clementi orbitals and assuming either a set of standard bond lengths[26] or using the experimental values.

Being aware of the limitations of the criterion of maximum overlapping and of possible difficulties in comparing overlaps in widely different kinds of bonds, it is advisable to restrict the application to related compounds and examine for them the relative changes between hybrids of various molecular environments. One expects then that all the molecules would be more or less similarly affected by the limitations of the method. The following section is therefore restricted to discussion of hybridization and construction of hybrids in various hydrocarbons.

Cyclopropane, for which the more elaborate calculations of Coulson and Moffitt[27] suggested bent bonds (*i.e.*, the bonds obtained by an off-line bond overlapping), was a suitable molecule for an initial examination of the suggestion of Craig (see ref 28) that simple calculations based on maximizing the bond overlap may lead to sufficiently good results. This has been shown to be the case by Coulson and Goodwin.[28] Instead of simply maximizing the sum of bond overlaps, such calculations can be improved, in particular by introducing appropriate scaling factors as suggested by Coulson (see ref 25). In hydrocarbons there are only two kinds of bonds, CC and CH, which have different amounts of bond energy per bond overlap. By scaling the bond overlaps, one compensates for the major part of the difference in bond energies, making the method more suitable for application. Such a modified method, the main features of which are discussed in the following sections, has been applied to a large number of hydrocarbons.

B. WORKED EXAMPLE

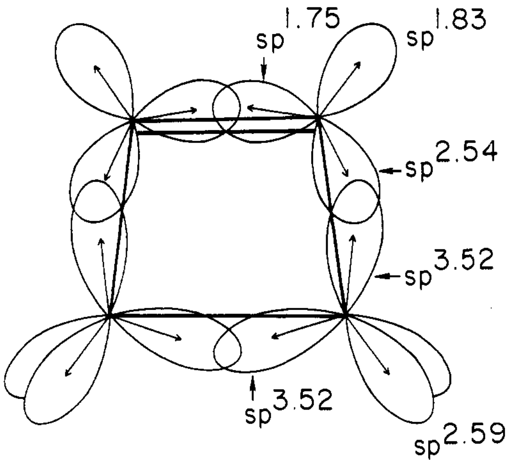

Figure 4. Cyclobutene: molecular skeleton with a schematic representation of the maximum overlap hybrids.

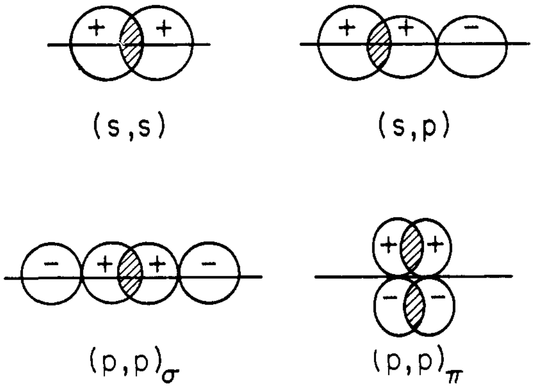

Figure 5. Basic overlap integrals of 2s and 2p orbitals.

As an example, let us consider cyclobutene (Figure 4). The numbering of atoms and the directions of various hybrids are illustrated in the figure. The atomic wavefunctions of the so-called "double-zeta" type of Clementi are used (eq 6). They

$$\phi_{2s} = -0.271\psi_{1s}(5.23) + 0.015\psi_{1s}(7.96) + 0.273\psi_{2s}(1.16) + 0.789\psi_{2s}(1.82) \qquad (6)$$
$$\phi_{2p} = 0.801\psi_{2p}(1.25) + 0.260\psi_{2p}(2.72)$$

are not quite so accurate as truly self-consistent field orbitals, but they are nearly so. Each orbital is a linear combination of normalized Slater-type functions, for which the corresponding exponent is indicated in parentheses. For the assumed CC single and double bonds of 1.535 and 1.34 Å, respectively, these functions give the following values for the basic overlap integrals (Figure 5).

basic overlap:	1.535 Å	1.34 Å
(2s, 2s)	0.360	0.447
(2s, 2p)	0.415	0.469
$(2p, 2p)_\sigma$	0.274	0.232
$(2p, 2p)_\pi$	0.264	0.346

Similarly for the CH bond lengths (assumed to be 1.09 Å), we have two basic integrals: $(1s_{\text{H}}, 2s_{\text{C}}) = 0.584$ and $(1s_{\text{H}}, 2p_{\text{C}}) = 0.508$. (For simplicity it is assumed here that all CH bonds are of the same length and that all CC single bonds are of the same length. When different bond lengths are assumed for

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(25) M. Randić and Z. Maksić, *Theor. Chim. Acta*, **3**, 59 (1965); Z. Maksić, L. Klasinc, and M. Randić, *ibid.*, **4**, 273 (1966).

(26) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(27) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(28) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963) (errata).

each kind, a set of basic overlap integrals will be different.) We write hybrids in the form

$$\begin{aligned} \psi_{12} &= a_{12}(\mathrm{s}) + b_{12}(\mathrm{p}_{12}) \\ \psi_{1\mathrm{H}} &= a_{1\mathrm{H}}(\mathrm{s}) + b_{1\mathrm{H}}(\mathrm{p}_{1\mathrm{H}}), \text{ etc.} \end{aligned} \qquad (7)$$

where (p_{12}) and $(\mathrm{p}_{1\mathrm{H}})$ are p orbitals directed toward atom 2 and H, the former of which in general deviate from the line joining atoms C_1 and C_2 by an angle δ_{12}. By decomposing the hybrid orbital ψ_{12} into components along and perpendicular to the C_1–C_2 line, we have

$$\psi_{12} = a_{12}(\mathrm{s}) + b_{12}\cos(\delta_{12})(\mathrm{p}_{\parallel}) + b_{12}\sin(\delta_{12})(\mathrm{p}_{\perp}) \qquad (8)$$

For the C_1–C_2 bond overlap, we then obtain

$$\begin{aligned} S_{12} = a_{12}a_{21}(\mathrm{s,s}) &+ [a_{12}b_{21}\cos(\delta_{21}) + a_{21}b_{12}\cos(\delta_{12})](\mathrm{s,p}) + \\ &b_{12}b_{21}\cos(\delta_{12})\cos(\delta_{21})(\mathrm{p,p})_{\sigma} + \\ &\qquad b_{12}b_{21}\sin(\delta_{12})\sin(\delta_{21})(\mathrm{p,p})_{\pi} \end{aligned} \qquad (9)$$

and for the bond overlap of C_1–H bond

$$S_{1\mathrm{H}} = a_{1\mathrm{H}}(1\mathrm{s_H},2\mathrm{s_C}) + b_{1\mathrm{H}}(1\mathrm{s_H},2\mathrm{p_C}) \qquad (10)$$

In the case of cyclobutene (observing the symmetry of the problem), the overall sum of bond overlaps which is scaled by the weighing factors k_{CC} and k_{CH} is then

$$S_{\mathrm{Total}} = k_{\mathrm{CC}}[S_{12} + 2S_{14} + S_{34}] + k_{\mathrm{CH}}[2S_{1\mathrm{H}} + 4S_{4\mathrm{H}}] \qquad (11)$$

The maximum of S_{total} is found by optimizing all the independent parameters. For instance, one can take on atom C_1 the coefficients a_{12} and a_{14}, which determines the third coefficient $a_{1\mathrm{H}}$ uniquely, but still leave the possibility of varying the deviation angle, say δ_{12}. The optimization of all the parameters will finally produce the hybrids sp^n of noninteger n which will maximize the suitably scaled sum of bond overlaps. With some practice in some 10–15 iterations, one can obtain results for the molecule of the size of cyclobutene. The results of such a calculation for cyclobutene are summarized below

$$\begin{array}{lll} \psi_{12} = 0.603(\mathrm{s}) + 0.799(\mathrm{p}) & \mathrm{sp}^{1.75} & S_{12} = 0.754 \\ \psi_{14} = 0.532(\mathrm{s}) + 0.847(\mathrm{p}) & \mathrm{sp}^{2.54} & S_{14} = 0.646 \\ \psi_{1\mathrm{H}} = 0.595(\mathrm{s}) + 0.804(\mathrm{p}) & \mathrm{sp}^{1.83} & S_{1\mathrm{H}} = 0.756 \\ \psi_{34} = 0.470(\mathrm{s}) + 0.883(\mathrm{p}) & \mathrm{sp}^{3.52} & S_{34} = 0.631 \\ \psi_{4\mathrm{H}} = 0.528(\mathrm{s}) + 0.849(\mathrm{p}) & \mathrm{sp}^{2.59} & S_{4\mathrm{H}} = 0.740 \end{array}$$

interorbital angles: $\theta_1 = 118°\,30'$, $\theta_4 = 106°\,30'$, $\theta_{4\mathrm{H}} = 112°\,45'$

deviation angles: $\delta_1 = 12°\,30'$, $\delta_4 = 10°$

In order to obtain some insight into the kind of information the more general hybrids offer, let us examine the results more closely. The simple description assumes at C_2 and C_4 sp^3 hybrids. Now we have hybrids with higher p content, which has as a consequence a decrease of the interorbital angle of the hybrids describing the four-membered ring. Such hybrids are therefore better suited to reduce the bond strain of the highly strained cyclobutene. The "excess" of s content is transferred to hybrids describing CH bonds, which are almost halfway between the sp^2 and sp^3 type, giving to this bond additional strength, which agrees with experience. At carbon atoms C_1 and C_2, the situation is more complicated, and it turns out not to be correct just to assume that the hybrids involved in the CC ring will tend to increase their p content in order to reduce the bond deviation angles. The bonds C_1–C_2 and C_1–C_4 are not even approximately similar, and it is not possible in advance to guess how the total s–p content should be redistributed so that the maximum overlap is achieved. It happens that the CH bond is to a large extent not affected by the presence of the CC double bond, which shows a strong tendency to achieve a high s content in spite of being in the small ring. This causes the other CC hybrid to have a high p content, and instead of the sp^2 hybrids we obtain $\mathrm{sp}^{1.75}$ and $\mathrm{sp}^{2.54}$, respectively. The results obtained for cyclobutene are quite representative and have been confirmed and extended by application to various other molecules with widely different structural groupings of atoms, the main features of which are summarized in the next sections.

III. Application of the Maximum Overlap Method to Hydrocarbons

A. CALCULATED HYBRIDS, BOND OVERLAPS, AND DEVIATION ANGLES

1. Cyclic Alkanes and Alkenes

For cyclopropane and cyclobutane (assumed planar),[19] it is expected that the hybrids involved in the ring formation have a high p content. In cyclopropene and cyclobutene, the symmetry is reduced allowing hybrids describing C—C and C=C to be different.[29] Work on methyl-substituted small rings has shown that the methyl group increases CC bond overlap, thus stabilizing the rings.[29a] The application of the method to larger molecules has been limited by the lack of knowledge of accurate molecular geometries. Among those studied are 1,5,9-tridehydro[12]annulene[30] and some cyclic olefins. We mentioned here the hybridization in 1,3,5-cycloheptatriene and related 1,3,5,7-cyclooctatetraene. For the hypothetical planar structure of these molecules, *negative* deviation angles of several degrees are obtained.[31] In contrast to outward bending of bonds in small rings, this inward bending in large cycles can be eliminated by puckering the molecular skeleton, finally leading to no bending and "straight" bonds for experimentally observed structures. The origin of puckering in these molecules, on which there were speculations,[32] can be accounted for without invoking more elaborated mechanisms.

2. Polycyclic Systems

A number of polycyclic hydrocarbons have been considered by the maximum overlap method. These include norbornane,[33] norbornene and norbornadiene,[34] barellene,[35] and adamantane (Figure 6).[36] Typical results are those of 2,3-dimethylene norbornene, illustrated in Figure 7 (ref 37). A comparison of the results between these molecules indicated that the hybrids in these molecules do not vary much for similar environments.

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(29) M. Randić and S. Borčić, *J. Chem. Soc., A*, 586 (1967). For effects on hybridization changes on the bond energies of C–C single bonds, see also J. E. Bloor and S. Gartside, *Nature (London)*, 184, 131 (1959).

(29a) M. Randić, D. Stefanović, and L. Klasinc, *Acta Chim. (Budapest)*, 50, 287 (1966); N. Trinajstić and M. Randić, *J. Chem. Soc.*, 5621 (1965).

(30) M. Randić and A. Rubčić, *Croat. Chem. Acta*, 43, 141 (1971).

(31) Z. Meić and M. Randić, *ibid.*, 40, 43 (1968).

(32) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, 1, 11, 117 (1967–68).

(33) M. Randić and D. Stefanović, *J. Chem. Soc. B*, 423 (1968); Z. B. Maksić and M. Eckert-Maksić, *Croat. Chem. Acta*, 42, 433 (1970).

(34) Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *J. Amer. Chem. Soc.*, submitted for publication.

(35) M. Randić and P. Matković, unpublished.

(36) Z. B. Maksić and L. Klasine, *Croat. Chem. Acta*, 40 101 (1968).

(37) M. Randić and A. Rubčić, unpublished.

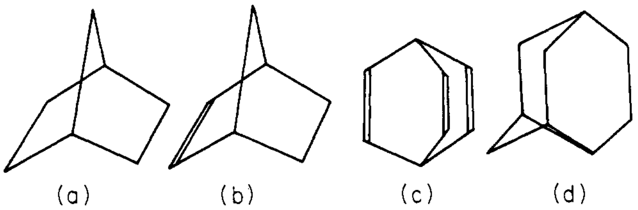

Figure 6. Polycyclic systems: (a) norbornane, (b) norbornene, (c) barellene, and (d) adamantane.

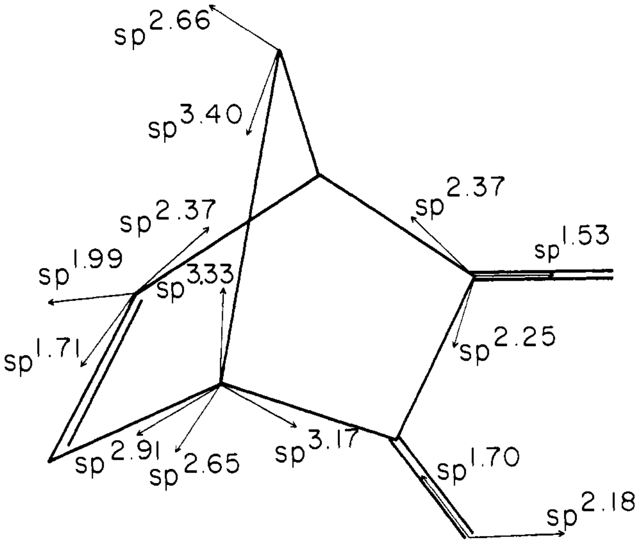

Figure 7. 2,3-Dimethylenenorbornene. Maximum overlap hybrids sp^n are schematically shown by arrows.

Some strain in bicyclo[2.2.1]heptane, -heptene, and -heptadiene rings is indicated by the magnitudes of several degrees for deviation angles at the bridge-carbon and bridgehead-carbon atoms.

3. Polycyclic Systems Having Small Rings

The composition of hybrids, the deviation angles, and the magnitudes of bond overlaps indicate how the skeletal strain of a polycyclic structure is distributed over the whole molecule. A number of molecules having a three- or four-membered ring incorporated in their structure have been examined, such as nortricyclene and tetracyclononane (Figure 8).[38] The results sometime show considerable bending of bonds outside three-membered rings (from 3 to 10°), indicating the dissipation of the strain over the remaining parts of the molecules. It is interesting that bond angles in several polycyclic molecules such as nortricyclene,[38] norcaradiene,[39] norbornene, and related molecules[34] have been well reproduced. However, such applications are of limited use, since it is not known to which extent such results depend on other contributions, like nonbonded repulsions, and may therefore be fortuitous.

4. Systems with Adjacent Small Rings

Molecules like bicyclo[1.1.1]pentane, cubane, tetrahedrane, and valence isomers of benzene (benzvalene, Dewar benzene,

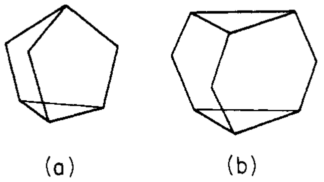

Figure 8. (a) Nortricyclene and (b) tetracyclononane.

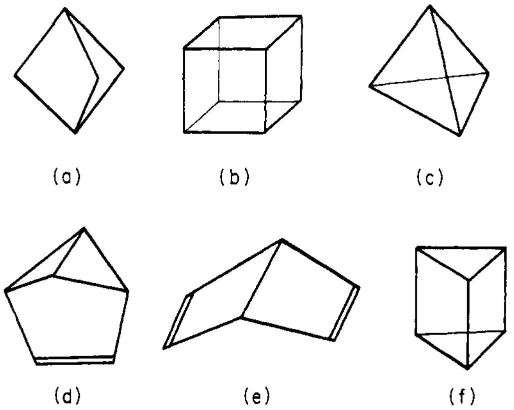

Figure 9. Hydrocarbons having adjacent small rings: (a) bicyclo[1.1.1]pentane, (b) cubane, (c) tetrahedrane, (d) benzvalene, (e) Dewar benzene, and (f) prismane.

and prismane (Figure 9)) are all characterized by having small rings adjacent to one another. This introduces severe constraints on hybrids involved in the corresponding bonds. In Table I are listed in ascending order selected CC bond overlaps of these molecules together with the composition of the hybrids forming the bonds, taken from ref 38 and 40. The most strained appears to be benzvalene should we judge from the presence of the smallest CC bond overlap appearing in the central-bridge bond. A comparison of CC bond overlaps in four-membered rings shows that planar cyclobutane is far from being the most strained system in the group. Slight puckering of cyclobutane skeleton introduced in order to relieve some H–H repulsions will reduce bond overlaps, but as seen from the Table I the smaller values are not prohibitive.

Table I

Bond Overlaps and the Corresponding Bond Hybrids for Various CC Bonds in Three- and Four-Membered Rings

	Bond overlap	*Molecule*	*Hybrids*
C_3	0.534	Benzvalene	$sp^{5.15}$–$sp^{5.15}$
	0.576	Tricyclobutane	$sp^{3.86}$–$sp^{3.86}$
	0.609	Spiropentane	$sp^{3.00}$–$sp^{3.90}$
	0.612	Tricyclopropylidene	$sp^{2.98}$–$sp^{3.78}$
C_4	0.618	Dewar benzene	$sp^{3.71}$–$sp^{3.71}$
	0.623	Bicyclopentane	$sp^{3.47}$–$sp^{3.63}$
	0.636	Cyclobutane (planar)	$sp^{3.47}$–$sp^{3.47}$
	0.641	Prismane	$sp^{3.03}$–$sp^{3.03}$

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(38) M. Randić, J. M. Jerkunica, and D. Stefanović, *Croat. Chem. Acta*, **38**, 49 (1966).

(39) Lj. Vujisić and Z. B. Maksić, *J. Mol. Struct.*, 7, 431 (1971).

(40) M. Randić and Z. Majerski, *J. Chem. Soc. B*, 2389 (1968).

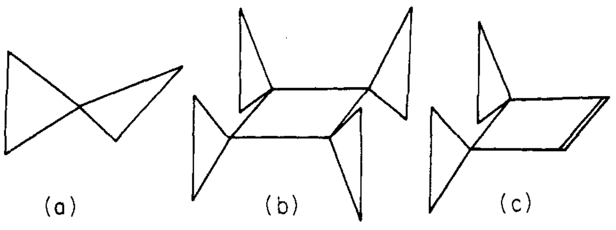

Figure 10. (a) Spiropentane, (b) tetracyclopropylidene, and (c) dispiro[2.0.2.2]oct-7-ene.

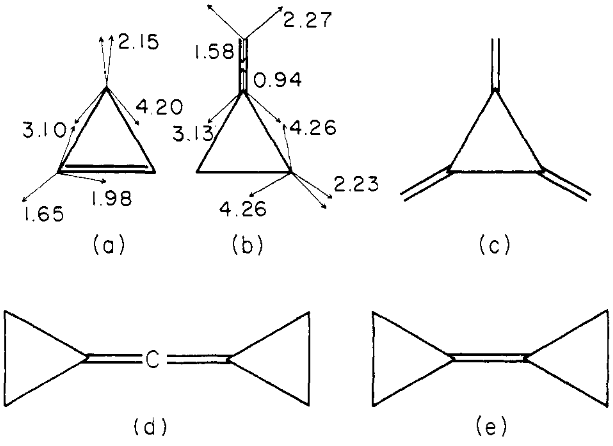

Figure 11. Small ring compounds having a C═C bond: (a) cyclopropene, (b) methylenecyclopropane, (c) trimethylenecyclopropane, (d) bisethanoallene, and (e) biscyclopropylidene.

5. Small Rings in Spiro Compounds and Systems with Exocyclic Double Bonds

Spiro junction of small rings introduces another kind of constraint. Among the several small rings spiro compounds investigated by the maximum overlap method are [38,41] spiropentane, tetracyclopropylidene, and dispiro[2.0.2.2]oct-7-ene (Figure 10). In spiropentane itself, the central carbon is symmetry forced into sp^3 hybridization. This gives an increase of the corresponding deviation angle from 22.5° in cyclopropane to about 25°. One may expect that spiropentane will therefore be more strained. However, the bond overlap is a better measure of bond strength than the angle of deviation. The forced sp^3 hybridization of spiro carbon in spiropentane ensures a relatively high s character in the corresponding hybrids and, consequently, produces a relatively high bond overlap. The C_3 ring in spiropentane is therefore relatively stronger than that in cyclopropane, and the same is true for the central ring in tricyclopropylidene.[41] Tetracyclopropylidene and dispiro[2.0.2.2]oct-7-ene have spiro carbons joining rings of different sizes. In these molecules the hybrids of both three- and four-membered rings compete for high p content in order to partly decrease the bending of the ring bonds. A similar situation arises in spiro[2.4]hepta-4,6-diene and spiro[2.4]hepta-2,4,6-triene, which consists of three- and five-membered rings. Also, these molecules allow for a delocalization of the electrons of the CC σ bond of the highly strained small rings to a suitably oriented π system of the other part of the molecule.

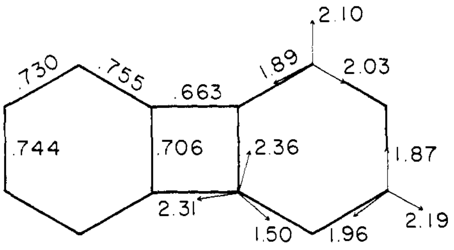

Figure 12. Biphenylene: molecular skeleton, showing a schematic representation of sp^n hybrids (right half of the diagram) and magnitudes of σ-bond overlap integrals (left half of the diagram).

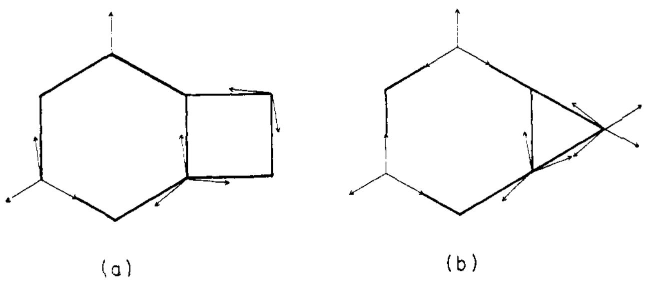

Figure 13. Fused ring systems: (a) benzocyclobutene and (b) benzocyclopropene.

Maximum overlap hybrids permit the separation of the part of the changes due to the specific structural environment of the spiro carbon from the contributions of possible delocalized interactions.[42]

The exocyclic double bond in methylenecyclopropane provides another kind of strain in three-membered rings. The simple sp^2 hybridization predicts interorbital angles of 120°, which would give a large deviation angle of 30° if attached to three-membered rings. When one allows the hybrids to adjust, by applying the method of maximum overlap, $d = 26°$ is obtained. The corresponding CC bond overlap (0.615) is among the largest values found in three-membered rings, clearly indicating that the exocyclic double bond has a stabilizing effect on the C_3 ring. Other molecules for which hybrids are available include trimethylenecyclopropane, bisethanoallene, and biscyclopropylidene and several of their derivatives (Figure 11).[43]

6. Systems with Fused Rings

Hybridization in biphenylene (Figure 12), benzocyclobutene, and related benzocyclopropene is of considerable interest (Figure 13). All these molecules are characterized by extremely unusual geometrical constraints forced by the in-plane fusion of already strained rings. The hybrids of highly strained four- (or three-) membered rings are directed toward the *inside* of the benzene ring; *i.e.*, the corresponding deviation angles are negative.[44] In addition, the fusion of the rings does not allow all hybrids to adopt simultaneously the most favorable orientation toward the molecular skeleton. This leads to asymmetrically bent bonds in which the deviation angles at the two ends

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[41] M. Randić and L. Jakab, *Croat. Chem. Acta*, **42**, 425 (1970); M. Randić and B. Goričnik, to be submitted for publication; and W. A. Bernett, *J. Chem. Educ.*, **44**, 37 (1967).

[42] M. Randić, A. Rubčić, and L. Klasinc, *Tetrahedron*, in press.

[43] M. Randić, J. M. Jerkunica, and L. Klasinc, *Theor. Chim. Acta*, **6**, 240 (1966); M. Randić and L. Jakab, *Croat. Chem. Acta*, **43**, 155 (1971).

[44] M. Randić and A. B. Maksić, *J. Amer. Chem. Soc.*, **93**, 64 (1971); M. Randić and Lj. Vujisić, to be published.

of a bond differ appreciably. In the special case when at one end there is no bending at all while at the other end a considerable bending occurs, as in the C_1–C_6 bond of benzocyclopropene, we have a half-bent or semibent bond, a new type of bond not previously met.

It is worthwhile to indicate the kinds of chemical bonds in hydrocarbons: bent bonds,[27] bent-out-plane bonds as found, *e.g.*, in prismane,[40] and twisted bonds where hybrid directions and the internuclear vector do not lie in the same plane.[25,44a]

B. CORRELATIONS BETWEEN THE HYBRIDIZATION OBTAINED BY THE MAXIMUM OVERLAP METHOD AND EXPERIMENTAL QUANTITIES

The bond overlaps and the hybrid s character calculated by the maximum overlap method have been correlated with such quantities as CC bond energies, vibrational stretching frequencies, proton chemical shifts in nmr spectra, spin–spin couplings constants $J(^{13}C\text{–}H)$ and $J(^{13}C\text{–}^{13}C)$, proton acidities, and C–H and C–C bond lengths. We briefly review the evidence which supports all the mentioned correlations.

1. *Vibrational Stretching Frequencies*

Intuitively, one expects that if a bond possesses larger overlap, due to larger s-orbital participation, the bond will be stronger and its stretching mode will be at higher frequency. Other factors are also important,[45] such as the ionic character, but as long as we are comparing bonds in similar molecules, one hopes they remain constant. That higher s content gives higher ir stretching frequency is demonstrated by CH stretching frequency of nortricyclene. CH hybrids of the three-membered ring in nortricyclene are calculated[38] to be $sp^{1.93}$, very close to idealized sp^2 hybridization assumed in benzene. The stretching of CH bonds appears at 3070 cm^{-1} in nortricyclene, approximately at the same place with the average of several CH stretching bonds of benzene. Similarly a normal C=C bond has a band at about 1670 cm^{-1}, while bands as high as 1780 and 1820 cm^{-1} have been reported for some small rings having exocyclic double bonds. The appreciable increase in the C=C stretching frequency as qualitatively correlated with the increase of the s character of the relevant hybrids and with the changes of bond overlaps for methylenecyclopropane, methylenebiscyclopropylidene, and molecules related to them.[43]

2. *Proton Chemical Shifts*

An attempt to correlate hybridization parameters calculated by the maximum overlap method and proton chemical shifts in hydrocarbons has been made.[40] A linear relationship between the values characterizing the chemical shifts and the hybrid exponent n (defining a sp^n hybrid of a CH bond) is obtained: $\tau = 5(n - 1)$. Although lacking a theoretical justification, the above correlation has some support in another empirical correlation found between τ and spin–spin coupling constants in some molecules and between τ and electronegativity.[46a] Also atomic populations for a number of molecules were correlated with the proton chemical shifts and gave a linear correlation.[46b] The above linear relationship between τ and n gave fairly good predictions in several applications, *e.g.*, norbornane,[40] norbornene, norbornadiene,[34] and 1,5,9-tridehydro[12]annulene.[30] However, in some molecules having CC double bonds and highly strained small rings, the simple relationship is less useful.[42]

3. *Spin–Spin Coupling Constants* *$J(^{13}C\text{–}H)$ and $J(^{13}C\text{–}^{13}C)$*

The $J(^{13}C\text{–}H)$ spin–spin coupling constants according to current assumptions provide a direct measure of s character of the hybrids describing CH bonds. The comparison with the experimental $J(^{13}C\text{–}H)$ can be made by adopting the empirical relationship of Muller and Pritchard:[47] $J(^{13}C\text{–}H) = 500a^2$ (in cps) where a is the coefficient of carbon 2s orbital in the hybrid describing CH bond. The satisfactory agreement in Table II strongly indicates that the maximum overlap method is suitable for evaluation of hybridization in hydrocarbons.

Table II

Hybrids Obtained by Maximum Overlap Method, CC Bone Overlap Integrals, and Experimental and Calculated $J(^{13}C\text{–}H)$

Molecule	*Hybrids*	*Overlap*	*J (exptl)*	*J (calcd)*	
Cyclohexane	$sp^{2.87}$	0.722	124	129	128
$H_2C{=}C(^{13}CH_3)_2$	$sp^{2.93}$	0.721	126	127	126
Cyclopentane	$sp^{2.82}$	0.724	128	131	131
Benzocyclobutene	$sp^{2.68}$	0.728	138	136	137
Cyclooctatetraene	$sp^{2.32}$	0.736	155	150	156
Allene	$sp^{2.20}$	0.739	168	156	162
Nortricyclene	$sp^{2.05}$	0.751	175	164	172
Acetylene	$sp^{1.25}$	0.771	249	223	248

If the variations in bond overlaps are taken into account, the simple proportionality between J and a^2 introduced by Muller and Pritchard is modified:[48]

$$J(^{13}C\text{–}H) = 1079a^2/(1 + S^2) - 55$$

For $J(^{13}C\text{–}^{13}C)$ coupling constants, a similar linear expression is found: $J(^{13}C\text{–}^{13}C) = 1020a_1{}^2a_2{}^2/(1 + S^2) - 8$. This is a modification of the expression of Frei and Bernstein,[49] who did not consider the variations in CC bond overlaps. The modified expressions give somewhat better agreement in most cases.

4. *Proton Acidities*

There is a good evidence that the acidity of hydrocarbons is considerably influenced by the state of hybridization of the C atom in question.[50] The s orbital, being of lower energy than

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(44a) P. G. Gassman, *Chem. Commun.*, 793 (1967).

(45) M. Scrocco, *Spectrochim. Acta* 22, 201 (1966); T. L. Brown and J. C. Puckett, *J. Chem. Phys.* **44**, 2238 (1966).

(46) (a) B. P. Daley and J. N. Schoolery, *J. Amer. Chem. Soc.*, **77**, 3977 (1955); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **90**, 3543 (1968).

(47) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1957); J. N. Schoolery, *ibid.*, **31**, 1427 (1959); M. Karplus and D. M. Grant, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1269 (1950).

(48) Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *Theor. Chim. Acta*, 22, 70 (1971); M. Randić, Z. Meić, and A. Rubčić, *Tetrahedron*, in press; M. Barfield, *J. Chem. Phys.*, **44**, 1836 (1966).

(49) K. Frei and H. J. Bernstein, *ibid.*, 38, 1216 (1963).

(50) E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 26.

the p orbital of the same principal quantum number, is more attractive for accommodating the negative charge of the carbanion concerned. The calculated and experimental acidities for selected nonconjugated hydrocarbons are shown in Table III. They lead to a linear relationship:[51] $pK = 83.1 - 1.3(s\%)$.

Table III

Hybrids Describing C–H Bonds Obtained by the Maximum Overlap Method, Corresponding s Character, and Calculated and Experimental Acidities

Molecule	*Hybridization*	*s character*	*pK (calcd)*	*pK (exptl)*
Acetylene	$sp^{1.29}$	43.6	25.1	25
Ethylene	$sp^{2.17}$	31.6	41.1	42
Cyclopropane	$sp^{2.40}$	29.4	44.0	44
Cyclopentane	$sp^{2.75}$	26.6	47.7	48
Cyclohexane	$sp^{2.87}$	25.8	48.8	49

5. Bond Energies

That a bond overlap is proportional to bond energy has been assumed in the procedure of scaling bond overlaps of different kinds of bonds. The simple proportionality $E = kS$, although correct to account for a presence of different kinds of bonds, does not adequately reflect the smaller variations within one kind of bond, in our case, CC bonds. A comparison between the bond overlaps and the bond energies for various types of single CC bonds of different hybridization (and different bond lengths) in cyclobutenes leads to a linear relationship: $E = 2.07kS - 81.3$, where k is the scaling factor for CC bonds.[29]

6. Bond Lengths

The well-known environmental changes in single CC bond lengths have been attributed to differences in hybridization of carbon atoms.[26,52] The bonds have been classified into sp^n–sp^m types (n, m being integers 1, 2, 3), and a rule was found that the CC single-bond distance decreases by 0.04 Å when n or m changes by one.[53] By applying the method of maximum overlap, such considerations are extended by not restricting n, m to integers. The results give a linear correlation between CC bond lengths and the corresponding bond overlaps.[54] The bond overlap depends on the amount of electron density in the region between the atoms forming the bond and is therefore expected to make a useful bond index. In Table IV are listed the calculated CC bond overlaps, the experimental CC bond lengths, and the corresponding maximum overlap hybrids for a selection of molecules. The linear relationship $\text{C–C (Å)} = -1.166S_{CC} + 2.298$ is obtained.

Table IV

Calculated CC Bond Overlaps and Bond Lengths According to the Maximum Overlap Method

Molecule	*Overlap*	*Hybrids*	*Bond length, Å*	
			Calcd	*Exptl*
Diacetylene	0.789	$sp^{1.15}$–$sp^{1.15}$	1.378	1.379
Vinylacetylene	0.737	$sp^{1.20}$–$sp^{2.23}$	1.439	1.448
Methylacetylene	0.718	$sp^{1.18}$–$sp^{3.01}$	1.460	1.459
Biphenyl	0.702	$sp^{2.19}$–$sp^{2.19}$	1.480	1.492
Propylene	0.685	$sp^{2.18}$–$sp^{3.01}$	1.500	1.501
Ethane	0.648	$sp^{3.20}$–$sp^{3.20}$	1.543	1.543

For CH bonds similar correlation gives $\text{C–H (Å)} = -0.869S_{CH} + 1.726$. The above bond overlap–bond length correlations can be used in an iterative procedure and applied to systems for which the variations in CC bonds are not known.[54] The above relationships between bond overlaps and bond lengths are expected to be obscured in highly strained systems with large deviation angles and in systems with delocalized electrons which give rise to alternations in bond lengths of their own. However, the results for biphenylene, where both of these effects are present, are encouraging.[44]

It should be mentioned that alternative descriptions and correlations are possible and have been suggested for correlating the experimental quantities such as the acidity, infrared stretching frequency, and bond length. Miller has argued, for example, that the properties of strained rings can be considered due to redistribution of electrons arising from the additional potential energy within the molecule. Any property that is proportional to hybridization should be proportional to the atoms contribution to the negative pole—the concept developed in his papers.[55] Similarly Bartell discusses the importance of nonbonded interactions on inferences of bond character from bond length. He concludes that structural effects attributed to conjugation, hybridization, and partial ionic character can be rationalized to a large extent in terms of nonbonded interactions.[55a]

C. COMPARISON OF MAXIMUM OVERLAP HYBRIDIZATION WITH RESULTS OF OTHER SEMIEMPIRICAL METHODS

There are several alternative approaches for an estimate of hybridization in molecules. They vary from empirical approaches based on experimental values of spin–spin coupling constants[47] $J(^{13}\text{C–H})$ or bond lengths[56] to methods which employ the results of rather elaborated molecular orbital calculations.[57–59] A comparison between maximum overlap hybrids and those obtained from semiempirical CNDO-SCF type calculations[57,59] is shown in Table V for cyclopropene and methylene cyclopropane. The agreement is quite satisfactory.

The maximum overlap method may be improved in several ways. For example, instead of making hybrids of the same atom orthogonal, one makes hybrids forming a bond orthogonal to other orbitals of the bonded atom.[60] Also by adopting a bond length–bond overlap correlation, one can, in an itera-

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(51) Z. B. Maksić and M. Eckert-Maksić, *Tetrahedron*, **25**, 5113 (1969).

(52) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **11**, 96 (1960); M. G. Brown, *Trans. Faraday Soc.*, **55**, 649 (1959).

(53) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); H. J. Bernstein, *J. Phys. Chem.*, **63**, 565 (1959). In this paper a relationship $l = 1.544 - 0.042 \cdot (6 - d - m)$, where sp^n and sp^m are the hybrids forming CC bond in question, was proposed. See also ref 26 and N. S. Ham, *Rev. Pure Appl. Chem.*, **17**, 159 (1961), for discussion of empirical regularities of CC bond lengths. It is interesting that the relationship of Bernstein, with some minor adjustments, can be extended to sp^n hybrids calculated by the maximum overlap method which are not limited to integer values of $n = 1, 2, 3$.

(54) Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.*, **92**, 424 (1970).

(55) I. J. Miller, *Tetrahedron*, **25**, 1349 (1959); *Aust. J. Chem.*, **24**, 457 (1971).

(55a) L. S. Bartell, *Tetrahedron*, **17**, 177 (1962).

(56) B. Bak and J. J. Led, *J. Mol. Struct.*, **3**, 379 (1969).

(57) C. Trindle and O. Sinanoǧlu, *J. Chem. Phys.*, **49**, 65 (1968); *J. Amer. Chem. Soc.*, **91**, 853 (1969).

(58) O. Sinanoǧlu, Yale University, personal communication, 1969.

(59) R. Polak, *Int. J. Quantum Chem.*, **4**, 271 (1970); R. Polak, *Chem. Phys. Lett.*, **9**, 630 (1971).

(60) C. A. Coulson, Oxford University, personal communication, 1970.

Table V

Comparison Between Hybrids Obtained from MO Treatments and Those Obtained by the Maximum Overlap Method for Cyclopropene and Methylenecyclopropane

Cyclopropane			*Methylenecyclopropane*		
Bond	*MO*	*Max overlap*	*Bond*	*MO*	*Max overlap*
1–2	$sp^{1.98}$	$sp^{1.86}$	1–2	$sp^{4.26}$	$sp^{3.78}$
1–3	$sp^{3.10}$	$sp^{2.85}$	1–3	$sp^{4.26}$	$sp^{3.95}$
3–1	$sp^{4.20}$	$sp^{3.99}$	3–1	$sp^{3.13}$	$sp^{2.70}$
1–H	$sp^{1.65}$	$sp^{1.56}$	3–4	$sp^{0.94}$	$sp^{1.18}$
3–H	$sp^{2.15}$	$sp^{2.34}$	4–3	$sp^{1.56}$	$sp^{1.77}$
			1–H	$sp^{2.23}$	$sp^{2.40}$
			4–H	$sp^{2.27}$	$sp^{2.13}$

tive procedure, calculate hybrids which give bond lengths consistent with the magnitudes of bond overlaps.[61] Possible improvement can perhaps be obtained by adopting a less diffuse hydrogen orbital,[62] taking, for example, $\zeta = 1.2$. There is sufficient evidence that the best atomic wavefunctions need not necessarily be good for describing atoms in molecules. The maximum overlap method is less sensitive to such changes since the scaling procedure in part compensates for it. Now from the theoretical point of view, one may ask how much the maximum overlap hybrids contribute to our knowledge of bonding in the organic molecules studied. To answer this question is difficult, since what we understand as "the knowledge of bonding" depends on the depth with which we wish to describe the systems. As is proper for semiempirical methods, the method of maximum overlap has been applied to a large number of molecules; and as demonstrated, the applications have led to several useful correlations and to a discovery of systematic trends in the values of the parameters *n*. It remains for organic chemists to find out how much of this series of comparisons might be interesting and revealing to them. As far as the basis of the method is concerned, the entire method of maximum overlap rests upon an intuitive notion that stronger bonds are produced when orbital overlap is larger. However, it is perhaps the time to consider the fundamentals of the method: How far can the method of maximum overlap be derived from the orthodox valence bond method? The entire concept of hybridization is a way of introducing configuration interaction into valence bond theory. For example, the tetrahedral configuration of carbon $C(t_1t_2t_3t_4)$ is, in fact, a linear combination of various genuine spectroscopic states arising from the configurations s^2p^2, sp^3, and p^4

$$C(t_1t_2t_3t_4) = a_1(sp^3,{}^5S) + a_2(p^4,{}^3P) + a_3(sp^3,{}^3D) + a_4(s^2p^2,{}^3P) + a_5(p^4,{}^1D) + a_6(sp^3,{}^1D) + a_7(s^2p^2,{}^1D) \quad (12)$$

where the constant a_i has prescribed values.[63] A full valence bond treatment would vary these constants so as to produce the minimum energy, and their values may well be different from those prescribed by the requirement of sp^3 hybridization. From this point of view, the significance of the results of the maximum overlap method is in providing the calculated values for the exponent *n* which are related to the parameters a_i. The future work will probably result in establishing the missing intimate relationship between the intuitive maximum overlap method and the rigorous valence bond formalism.

An interesting paper by Bartlett and Öhrn, discussing the quantitative nature of the concept of maximum overlap, has very recently appeared.[64] Although minimum energy and maximum overlap are not equivalent, it is possible to obtain the same wavefunctions using the latter criterion, which is computationally exceedingly simpler than the application of the variational principle and the computation of difficult molecular integrals, if the corresponding operator associated with the two district approaches commute. By examining this in detail, Bartlett and Öhrn discuss the situations when it is possible to obtain approximate wavefunctions solely from a diagonalization of the overlap matrix and conclude that "for predominately covalent systems, there is, at least, some reality to the maximum overlap-molecular orbital functions" and that therefore these are likely to be a convenient starting set of orbitals for more sophisticated calculations.[64]

IV. Application of the Maximum Overlap Criterion to Molecules with Several Different Atoms

A difficulty in extending the maximum overlap method to molecules with several different atoms is that in such cases other factors, like electronegativity or ionic character, are of importance.[65] If an atom carries a net positive charge, the orbital will be contracted and the overlap may decrease at constant distance. In ionic systems or strongly polar ones (*e.g.*, LiF), the actual sizes of the atoms can be reversed as a result of polar migration of charge. In such cases we need to know the orbital exponents in the atomic orbitals, or how they depend on the effective charge. This is also of importance in other semiempirical methods; however, the problem has not been sufficiently investigated. It seems therefore that the maximum overlap method is of most use when dealing with largely covalent situations. An application of the maximum overlap method in its present form to systems with lone pairs, not participating in the competition for s-orbital content, would result in the lone pairs with unacceptably high p content. However, lone pairs in NH_3 and H_2O possess the maximal amount of s character[66] and could frequently be considered wholly as s orbitals.[67]

Several papers have discussed the molecular geometry and molecular angles by considering overlaps. Generally, there is a fundamental difficulty in predicing bond lengths. This, of course, does not contradict the existence of bond overlap–bond length correlation. Since the criterion of maximum overlapping deals only with attractive forces and says nothing about the repulsive forces that operate in a bond, it is not able to predict bond lengths, which depend on an equilibrium between these two sets of forces. Because it is necessary to assume the geometrical shape of a molecule before applying the maximum overlap method, this does not mean that the method is not capable for discussing lengths. The situation is

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(61) M. Randić, Lj. Vujisić, an Z. B. Maksić, to be published; see also ref 34.

(62) F. Jordan, M. Gilbert, J. P. Malrieu, and U. Pincelli, *Theor. Chim. Acta*, **15**, 211 (1969).

(63) J. K. Wilmhurst, *J. Chem. Phys.*, 30, 889 (1959).

(64) R. J. Bartlett and Y. Öhrn, *Theor. Chim. Acta*, 21, 215 (1971).

(65) H. H. Voge, *J. Chem. Phys.*, 4, 581 (1936). See also very recent publication: G. Howat and B. C. Webster, *J. Chem. Soc. A*, 13 (1971), in which atomic Hartree–Fock calculations are presented for the carbon atom in methane, and the most favorable description is found with carbon in ${}^5S$ term of an sp^3 configuration.

(66) R. F. W. Bader and G. A. Jones, *J. Chem. Phys.*, 38, 2791 (1963); *Can. J. Chem.*, 41, 586, 2251 (1963); M. Klessinger, *J. Chem. Phys.*, 43, S 117 (1965). See also R. McWeeny and G. Del Re, *Theor. Chim. Acta*, 10, 13 (1968).

(67) V. M. Volkov, *Zh. Neorg. Khim.*, 8, 167, 1820 (1963).

analogous to calculations on delocalized π-electron systems using the Hückel method. One starts with a standard set of bond lengths and uses a bond order–bond length curve (for π-electron systems) or bond overlap–bond length correlation (for σ-electron systems) to obtain the information on the variations of the calculated bond lengths from the assumed standard values. Correct (to $\pm 2°$) bond angles were reported[68] for H_2O and NH_3, and an explanation of why these molecules have larger bond angles than H_2S and PH_3 was suggested.[69] Maximum overlap criterion has also been applied to discussion of configurations in such molecules[70] as UF_2 and UF_3. However, all such conclusions have to be taken with due caution as it remains to be understood better whether or not in such systems the directions of hybrids follow the directions of bonds.[71] Finally, the idea that hybridization depends on the geometry has long been acknowledged in discussions of molecular vibrations and potential force fields.[72] More recently, Mills has elaborated these lines and introduced the physically very attractive "hybrid orbital following" potential field, an improvement on the well-known Urey–Bradley force field, in which a change of geometry during vibration is followed by a change in the hybridization and is taken into account by off-diagonal force constants adequately.[73] There is also a report on a direct application of the maximum overlap method to force constant calculations in molecules[74] like CH_4, SiH_4, CF_4, and BF_3. Other applications of the maximum overlap method include electron-deficient species[75] CH_5^+ and B_2H_6, and an attempt to discuss bonding in cis and trans square-planar complexes[76] and in eight-coordinated square-antiprism complexes.[76a]

The applications of overlap criteria in heteroatomic systems reveal some difficulties since here the relationship between the overlap and the bond energy is no longer simple. The reason for the failure of the overlap integral as a measure of bond strength in diverse molecules is that although it accounts for the amount of the overlap charge it does not account for the strength of its attraction to bonded atoms.[77] Extension to problems where d as well as s and p orbitals arise leads to the problem of finding appropriate weighing factors. Unless they are tested on several molecules, there is a danger that by adjusting them to an individual case other contributions which may be important, like bond polarity or charge migration, may be masked.

V. Concluding Remarks

Besides being useful for approximate description of bonding in molecules, hybrids are also useful in the analysis of available complex wavefunctions resulting from elaborated semiempirical or more exact calculations. Therefore, a possible use of maximum overlap hybrids is their incorporation from the beginning in the construction of more exact wavefunctions.[78] However, we should stress that the description of molecular structures in terms of hybrids has not been meant to "compete" with more detailed and ambitious approaches. The comparisons with the calculations on several small hydrocarbons has been introduced only to indicate the degree of agreement between the simple hybrid description and more elaborate work. The maximum overlap method is suitable for application on larger and less symmetrical molecules, having similar kinds of bonds, for which for some time in the future no other suitable methods will be available. In connection with this, we may quote the general remark concerning the use of overlap criteria, made by Peters,[77] and valid for the maximum overlap method: "the general impression is that the overlap integral may be useful in determining the strength of a set of similar bonds, but that it lacks flexibility for dealing with the general bonds." And finally, maximum overlap hybrids are not only intended for a temporary use. We are inclined to believe that the hybrid description is going to remain an important description of molecules, and presents an evolution of the classical chemical structural formulas which have been limited to interpretation in terms of by now obsolete sp^3, sp^2, and sp hybrids.

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