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# SYMMETRY, HYBRIDIZATION AND BONDING IN MOLECULES†

ZVONIMIR B. MAKSIĆ
Theoretical Chemistry Group, The "Rudjer Bošković" Institute, 41001 Zagreb, Yugoslavia,
and The Faculty of Natural Sciences and Mathematics, The University of Zagreb,
Marulićev trg 19, 41000 Zagreb, Yugoslavia

**Abstract**—Brief historical review of the applications of symmetry arguments in interpreting the electronic and geometric structures of molecules is given. The hybridization of atomic orbitals is thoroughly discussed. It was shown that hybridization model describes directional features of covalent bonding and a number of other properties which are not directly related otherwise. This versatility in rationalizing a large number of experimental data of different kinds and a high interpretative power give to the model some semblance of truth. The model's apparently good reflection of molecular properties could be traced to the fact that hybrids conform with the local symmetry of an atom in a molecular environment. An analogy between the hybridization model and crystal field theory is found. The epistemological role of the hybridization is stressed. It provides a bridge between the most elementary first principles of quantum mechanics and the concept of a chemical bond, which is a basic tenet of the phenomenological theory of molecules.

> Symmetry, as wide or as narrow as you may define its meaning, is one idea by which man through ages has tried to comprehend and create order, beauty and perfection.
>
> *H. Weyl*

## INTRODUCTION

Symmetry is one of the basic principles which helps a great deal in our efforts to understand the universe. It underlies, for example, the conservation laws of linear and angular momenta, which are a consequence of the homogeneity and isotropy of space. Similarly, the conservation of energy can be derived from the invariance of the equations of motion to the shift in time[1]. Elementary particles follow specific symmetry rules. Hence, it is not surprising that symmetry gives a deep insight into the structure of matter. It has strongly influenced the development of the theory of the electronic structure of molecules and crystals, particularly after the advent of quantum mechanics. Indeed, symmetry has revealed some of the very fundamental facets of chemical bonding. It found especially wide and important applications in spectroscopy by determining the so-called selection rules. Wigner writes, ". . . The actual solution of quantum mechanical equations is, in general, so difficult that one obtains by direct calculations only crude approximations to the real solutions. It is gratifying, therefore, that a large part of the relevant results can be deduced by considering the fundamental symmetry operations"[2]. He mentioned additionally that almost all rules of spectroscopy follow from the symmetry of the problem.

Symmetry arguments were an important guide even in the prequantum era. It is well known that Pasteur, van't Hoff and Le Bel recognized in the last century a close connection between the optical activity and asymmetry. It is also noteworthy that the mathematical tools necessary for a description of crystal symmetry (230 three-dimensional space groups, 32 crystallographic point-groups and 14 Bravais lattices) were coined before the end of the 19th century, that is to say, well ahead of the discovery of the X-ray method[3]. It is also interesting to mention that in 1883, some 30 years before the X-ray diffraction technique was actually invented, an English scientist by the name of Barlow assigned quite correctly the structure of a number of crystals by using abstract group theory[4]. However, the paramount importance of symmetry in gripping the basic features of the microworld was fully realized only after the rise of quantum theory, as noted above. The role of the newly developed spectroscopic techniques and of molecular (and crystal) structure determination methods in the 1950s should not be underestimated in this respect.

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† Dedicated to Professor Linus Pauling—Prometheus of the modern chemistry—on the occasion of his 85th birthday.

Symmetry entered quantum chemistry via the classical paper of Bethe[5] on the term splitting of atoms and ions imbedded in crystals. That was the beginning of crystal field theory, which was subsequently developed by Van Vleck[6,7] and others[8,9]. In spite of the fact that the influence of ligands was mimicked by point charges forming the electrostatic field exerted on central atomic states, crystal field theory was highly effective because of its inherent symmetry content. Therefore, the following citation of Moffitt and Ballhausen[10] seems to be in place here: "It will be a long time before a method is developed to surpass in simplicity, elegance and power that of crystal field theory. Within its extensive domain it has provided at least a deep qualitative insight into the behaviour of a many electron system." The crystal field theory was later replaced by the ligand-field molecular orbital theory, which properly takes into account covalency (overlap) effects[11–13]. Its simplified version named the angular overlap method (AOM), is particularly useful due to its great applicability[14]. Molecular orbital theory was put forward predominantly by Mulliken[15,16]. The molecular orbitals (MO) wavefunctions, which describe the one-electron charge distribution over the whole domain of a molecule, enjoy wide popularity due to the ease of their computational implementation. They belong to the irreducible representations of the respective point-symmetry group[16] and are a convenient vehicle for the interpretation of molecular spectra. The MO theory has faithfully served chemistry for more than 50 years. It is far beyond the scope of this article to review all fields of its application. We shall mention instead their use in rationalizing concerted chemical reactions, which resulted in the well-known orbital symmetry conservation rules[17], thus establishing the intimate relationship between the symmetry properties of reactants and products.

The complicated vibrations of nuclei in molecular systems can be simplified and systematized by the use of symmetry and its mathematical tool-group theory. The pioneering work in this field was done by Wigner[18] and Bright–Wilson[19,20]. The motion of nonrigid molecules is even more intricate, but the use of symmetry is illuminating, as shown by the inspired paper of Longuet–Higgins[21] and by other researchers[22,23]. The rigorous calculation of wavefunctions in moderately large molecular systems is an extremely difficult task despite the exploitation of powerful high-speed computers. This applies particularly if the electron correlation is estimated as accurately as possible. Significant breakthrough in the computation of energy matrix elements was recently achieved by the use of unitary group representations[24,25]. Last but not least, submolecular particles like electrons are identical, thus exhibiting permutational symmetry properties[26,27].

The rough and incomplete historical sketch presented above conclusively shows that symmetry is of tantamount importance in tackling problems of the electronic structure of molecules. It is obviously an invaluable tool in treating properties of crystals where the number of particles, i.e. the complexity of problems, is immensely increased[28]. Thus, symmetry and group theory will always remain one of the most powerful weapons in the theoretical arsenal.

There is one aspect which was not discussed so far. The building blocks of molecules and crystals are atoms. This point of view is close to chemical intuition because structural formulas of compounds are composed of atomic symbols. We usually say that a water molecule is built from two hydrogen atoms and one oxygen atom. We rarely describe this molecular system as an ensemble of two protons, a nucleus with charge $+8|e|$ (involving 16 nucleons) and 10 electrons. There must be a good reason for this attitude. Indeed, there is a comprehensive evidence that atoms retain their identity after the formation of chemical bonds. They are not identical to atoms *in statu nascendi*, but are somewhat perturbed by their chemical environment instead. Atoms in molecules are best described as *modified atoms*. One of the apparent changes is a descent of symmetry. Free atoms are spherically symmetric, while their local symmetry, dictated by the nearest neighbours, is significantly lower in the hierarchy. It is clear that the local atomic wavefunctions (or densities) will be given as a linear combination of the free-atom eigenfunctions. This was ingeniously recognized by Pauling as early as 1931 and published in a paper[29] which is another milestone in the history of the theory of chemical bonding. Pauling's hybrid orbitals paved a large avenue called the valence bond (VB) theory, which dominated early quantum chemistry. To be fair, one should mention that hybrids were almost simultaneously invented by Slater also[30]. However, it was Pauling's work which conclusively showed their efficacy in rationalizing molecular and crystal structures. It turned out that hybridization is a simple and intuitively appealing model possessing at the same time a very high content of chemical information providing an important link between the fundamental quantum concepts, and empirical knowledge gathered by experimental chemists. Since the renewed interest might well lead to a renaissance of hybridization and VB theory[31–56], we shall dwell on the former in some more detail in this article, which is a review in a sense that it covers a rather extensive field of applications of hybridization. However, inclusion of all the literature on this topic is not intended. We shall see that the hybridization concept yields a rich harvest of chemically relevant results and penetrating conclusions. Theory will be presented on the elementary level, which permits easy digestion by a nonspecialist. In particular, only spatial wavefunctions will be considered. The spin parts can be obtained by using the formalism of the permutation symmetry group[26,27].

## HYBRIDIZATION OF ATOMIC ORBITALS

> If you know a thing, it is simple; if it is not simple, you don't know it.
>
> *Oriental proverb*

### *Atomic orbitals*

Description of the hydrogen atom and the related hydrogen-like ions requires solution of the corresponding Schrödinger equation involving the spherically symmetric central potential $V(r) = -e^2Z/r$. The symmetry of the problem is best exploited by the use of the polar coordinate system (Fig. 1). Then the wavefunction can be written as a product of the radial and angular parts:

$$\Phi_{nlm} = R_{nl}(r)Y_{lm}(\vartheta, \varphi), \tag{1}$$

where $n$, $l$, $m$ denote the quantum numbers[57]. This is a remarkable result because the well-known spherical harmonics $Y_{lm}(\vartheta, \varphi)$ depend only on the symmetry of the central field and not on its details. The latter are stored in the radial wavefunction $R_{nl}(r)$. Consequently, the angular $Y_{lm}(\vartheta, \varphi)$ functions can be determined once and for all and in fact that was done a long time ago. A few lowest spherical harmonics are given in Table 1. The one-electron function of the form (1) which describes average behaviour of an electron in the atom is called an atomic orbital. It has a strict meaning only in one-electron atoms (ions). In many-electron atoms the electrons do not move independently. They permanently interact and concomitantly the total wavefunction $\Psi$ depends on their relative positions. It is gratifying, however, that a fairly realistic picture is obtained by the independent-electron approximation in the familiar Hartree–

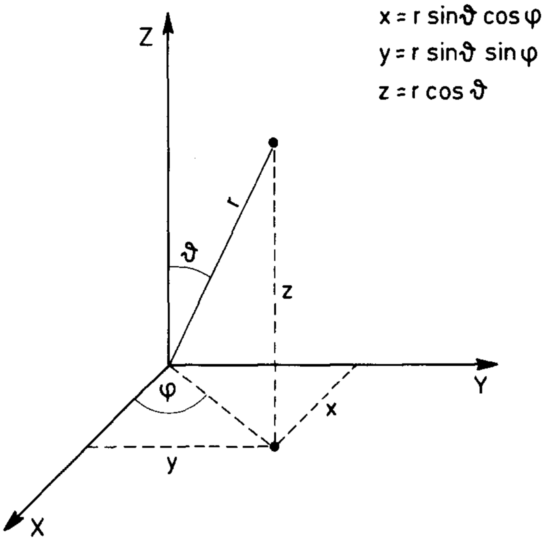

Fig. 1. Relation between Cartesian and polar coordinates.

Table 1. The angular parts of the hydrogen-like atom wavefunctions

| Symbol | Spherical harmonic |
|---|---|
| $Y_{00} = s$ | $\frac{1}{2}\sqrt{\pi}$ |
| $Y_{10} = p_0$ | $(\sqrt{3}/2\sqrt{\pi}) \cos \vartheta$ |
| $Y_{11} = p_1$ | $(\sqrt{3}/2\sqrt{2\pi}) \sin \vartheta e^{i\varphi}$ |
| $Y_{1-1} = p_{-1}$ | $(\sqrt{3}/2\sqrt{2\pi}) \sin \vartheta e^{-i\varphi}$ |
| $Y_{20} = d_0$ | $(\sqrt{5}/4\sqrt{\pi})(3 \cos^2 \vartheta - 1)$ |
| $Y_{22} = d_2$ | $(\sqrt{15}/4\sqrt{2\pi}) \sin^2 \vartheta e^{i2\varphi}$ |
| $Y_{2-2} = d_{-2}$ | $(\sqrt{15}/4\sqrt{2\pi}) \sin^2 \vartheta e^{-i2\varphi}$ |
| $Y_{21} = d_1$ | $(\sqrt{15}/2\sqrt{2\pi}) \sin \vartheta \cos \vartheta e^{i\varphi}$ |
| $Y_{2-1} = d_{-1}$ | $(\sqrt{15}/2\sqrt{2\pi}) \sin \vartheta \cos \vartheta e^{-i\varphi}$ |

Fock method. The single electron moves in the average electrostatic field of all the remaining particles and the total wavefunction is obtained in the iterative self-consistent fashion[57]. It should be recalled also that $\Psi$ satisfies the antisymmetry condition and its simplest form is given by the single determinant

$$\Psi(1 \ldots n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \Phi_1(1) & \cdots & \Phi_1(n) \\ \vdots & & \vdots \\ \Phi_n(1) & \cdots & \Phi_n(n) \end{vmatrix}. \tag{2}$$

Hence, the orbital concept is preserved albeit it holds only to a certain limit. It is important to emphasize also that all electrons are equally distributed over all orbitals in the total wavefunction $\Psi(1 \ldots n)$ (2). In spite of their approximate nature, atomic orbitals (AOs) have an important heuristic role in chemistry and provide a convenient basis for quantum-chemical calculations on molecules. While the best atomic orbitals are obtained by the self-consistent field approach, a reasonable representation is offered by the concept of nuclear screening. The interelectronic repulsion can be approximated by the scaling of the nuclear charge $Z$, which assumes then the $Z - S$ form. Here $S$ denotes screening. It can be determined either variationally or roughly, for certain groups of electrons, by using the well-known Slater rules[57]. We shall not be concerned with the specific form of the radial $R_{nl}(r)$ parts of AOs because the symmetry properties are incorporated in their angular parts. It should be noted in passing, however, that AOs presented in Table 1 have defined well both the angular momentum and its projection to the $Z$ axis. On the other hand, the most salient feature of covalent bonds is their directionality in space. If chemical bonding is to be interpreted on an orbital basis, then the directional nature of the AOs should be emphasized as much as possible. Is there an equivalent basis set which is better in this respect? The answer to this question is positive because (a) the AOs belonging to the same subshell ($Y_{lm}$, where $m = -l, \ldots, +l$) are degenerate, and (b) the total wavefunction $\Psi$ (2) is invariant to all unitary transformations of orbitals $\Phi_i$. It turns out that by making simple linear combinations of $Y_{lm}$ and sacrificing the magnetic quantum number $m$, one obtains AOs with favourable directional properties. They are listed in Table 2 and depicted in Fig. 2. The shaded lobes in the latter correspond to domains where AOs assume positive values. It should be

Table 2. Directional atomic orbitals

| Symbol | Orbital |
|---|---|
| $s$ | $\frac{1}{2}\sqrt{\pi}$ |
| $p_X$ | $\frac{1}{2}(p_1 + p_{-1}) = (\sqrt{3}/2\sqrt{\pi}) \sin \vartheta \cos \varphi$ |
| $p_Y$ | $-\frac{1}{2}(p_1 - p_{-1}) = (\sqrt{3}/2\sqrt{\pi}) \sin \vartheta \sin \varphi$ |
| $p_Z$ | $p_0 = (\sqrt{3}/2\sqrt{\pi}) \cos \vartheta$ |
| $d_{X^2-y^2}$ | $\frac{1}{2}(d_2 + d_{-2}) = (\sqrt{15}/4\sqrt{\pi}) \sin^2 \vartheta \cos 2\varphi$ |
| $d_{XY}$ | $-\frac{1}{2}(d_2 - d_{-2}) = (\sqrt{15}/4\sqrt{\pi}) \sin^2 \vartheta \sin 2\varphi$ |
| $d_{XZ}$ | $\frac{1}{2}(d_1 + d_{-1}) = (\sqrt{15}/2\sqrt{\pi}) \sin \vartheta \cos \vartheta \cos \varphi$ |
| $d_{YZ}$ | $-\frac{1}{2}(d_1 - d_{-1}) = (\sqrt{15}/2\sqrt{\pi}) \sin \vartheta \cos \vartheta \sin \varphi$ |
| $d_{Z^2}$ | $d_0 = (\sqrt{5}/4\sqrt{\pi})(3 \cos^2 \vartheta - 1)$ |

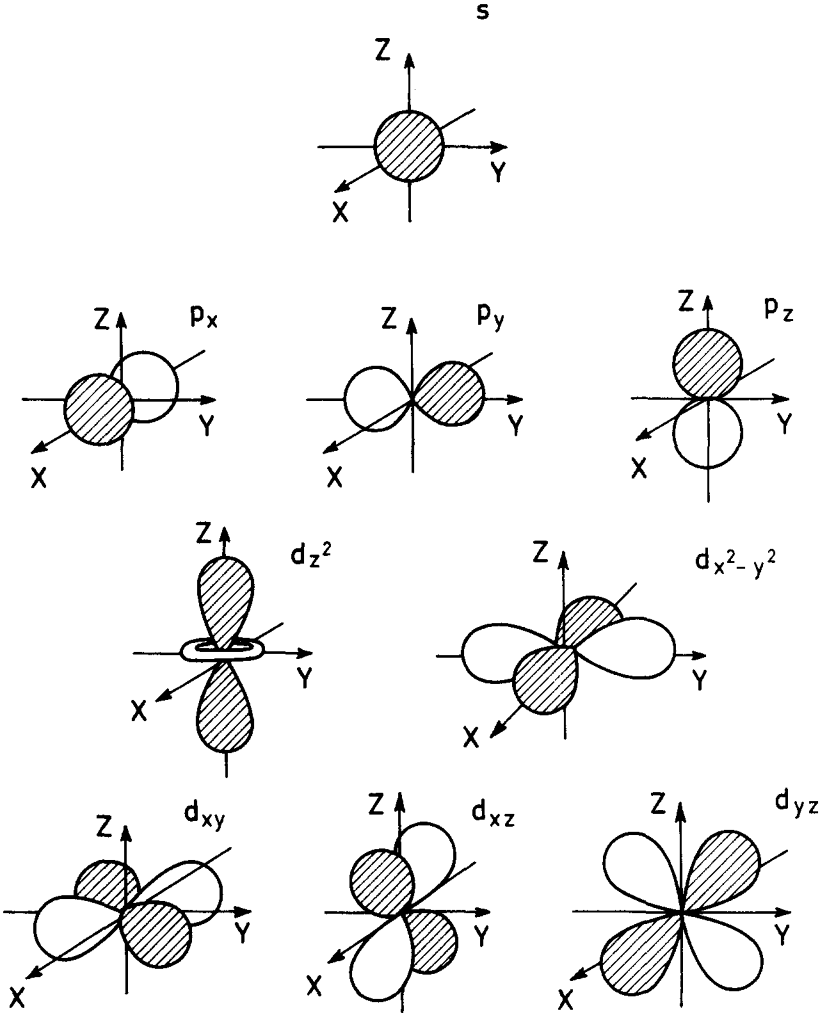

Fig. 2. Schematic representation of the angular parts of a central potential one-electron wavefunction.

mentioned that subscripts in the spatial representation of AOs, e.g. $p_X$, $p_Y$, $p_Z$, etc., yield immediately the functional dependence of the orbital on Cartesian coordinates. The simple unitary transformations indicated in Table 2 illustrate very nicely the process of adaptation of the basis set for the description of the chemical bonding. It will appear that the basis of AOs presented in Table 2 is very useful for this purpose, but it does not suffice, particularly for tetracoordinate atoms. This will be discussed in some more detail in the next section.

### *Hybrid orbitals*

One of the most remarkable facets of molecules (apart from some exceptional cases) is the relative rigidity of their geometric structures. It is this rigidity which permits the widespread use of molecular "ball-and-stick" models in chemistry instead of, for example, the liquid-drop model, which would be completely inadequate. One of the main aims of theoretical chemistry is to rationalize the directional character of covalent bonds. The most attractive and intuitively appealing way to do this is the use of the atomic orbital concept. The underlying idea is that atoms retain their identities to a considerable extent within the molecule, and is close to chemical experience. Indeed, notions of atoms and bonds are of central importance for phenomenological descriptions of properties of myriads of molecules. It is empirically known that bonds between a given pair of atoms have similar properties. For instance, the bond energy in $H_2O$ is 118 kcal/mole, which can be compared with the corresponding O—H value of 112 kcal/mole in $CH_3OOH$. Hence, the bond energies exhibit the characteristic additivity at least to a first approximation. Furthermore, certain stretching vibrational frequences are fairly constant for a given bond type (e.g. the CH frequency is ~2900 $cm^{-1}$ and the OH frequency is ~3600 $cm^{-1}$) which is used for analytical purposes to identify the characteristic groupings of atoms within complex molecules. The bond distances between the atoms, which are characterized by their coordination numbers, do not vary much as a rule (for example, the C—H bond attached to the tetracoordinated carbon atom is roughly ~1.10Å in a large number of organic compounds). Is there any relation between the relative constancy of a variety of bond properties and their transferability across the families of related molecules and directional features of covalent bonds? Anticipating conclusions of the forthcoming discussion we can say that there is a close connection between these properties although they seem to be unrelated at the first sight.

Empirical knowledge shows that many properties of covalent bonds are nearly constant in similar moieties, suggesting that the total electronic charge can be approximately partitioned into pairs of electrons which are almost completely localized in the region of each bond. The idea that bonds are formed by shared electron pairs was first put forward by Lewis[58] as early as 1916. The quantum-mechanical basis and proper interpretation of the Lewis postulate was given by Heitler and London in their benchmark paper[59], which represents the birthday of the valence bond (VB) theory and of quantum chemistry at the same time. A pair of bonding electrons in the bond A—B is described in this approach by the spatial wavefunction

$$\Psi_{AB}(1, 2) \sim [\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)], \tag{3}$$

where $\psi_A$ and $\psi_B$ are atomic orbitals centered on the nuclei A and B, respectively. The spins of electrons placed on $\psi_A$ and $\psi_B$ are opposite and the spin function of the form $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ is omitted for the sake of simplicity. Consider the simple VB treatment of bonding in the $H_2S$ molecule. The electron configuration of sulfur is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^4$. Neglecting the core formed by the nucleus and full electron shells one obtains the configuration of valence electrons $(3s)^2(3p_Z)^2(3p_X)(3p_Y)$, where the AOs $3p_X$ and $3p_Y$ are populated by an electron each possessing the same spin (Hund's rule). Since the number of unpaired spins determines valency of the atom in question[59], sulfur can bind two hydrogens. The bond strength is roughly given by the exchange integral, which in turn is approximately proportional to the corresponding overlap integral between the $\psi_A$ and $\psi_B$ AOs[59]. Hence, according to the *maximum overlap criterion*[29,30] the hydrogen $1s_H$ functions should be placed on the $X$ and $Y$ axes at some optimal distance, implying that the H—S—H angle is 90° (Fig. 3). This is in reasonable accordance with the experimental value of 92.2°, indicating that the simple VB picture offered by the spatial part of the total wavefunction

$$[\psi_{3p_X}(1)\psi_{1sH_1}(2) + \psi_{3p_X}(2)\psi_{1sH_1}(1)][\psi_{3p_Y}(3)\psi_{1sH_2}(4) + \psi_{3p_Y}(4)\psi_{1sH_2}(3)]$$

is essentially correct. The bond angles in $H_2Se$ (91°) and $H_2Te$ (89.5°) can be explained by the same token. By reversing the argument, one can say that two hydrogen atoms approaching a sulfur atom diminish its symmetry. The $Z$ axis, unspecified otherwise, now assumes a direction perpendicular to the plane of the HSH atoms. The $3p$ subshell is split by the descent of symmetry. The $3p_Z$ orbital is populated by the lone pair, while $3p_X$ and $3p_Y$ functions, remaining degenerate, can be used for chemical bonding with hydrogens forming two equivalent S—H bonds. It is important to emphasize that good agreement with experiment was obtained by

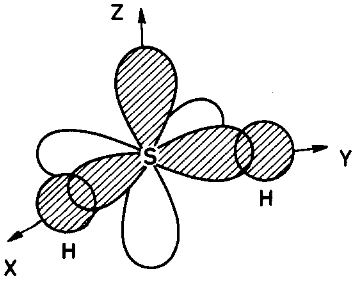

Fig. 3. Simple bonding scheme in the $H_2S$ molecule.

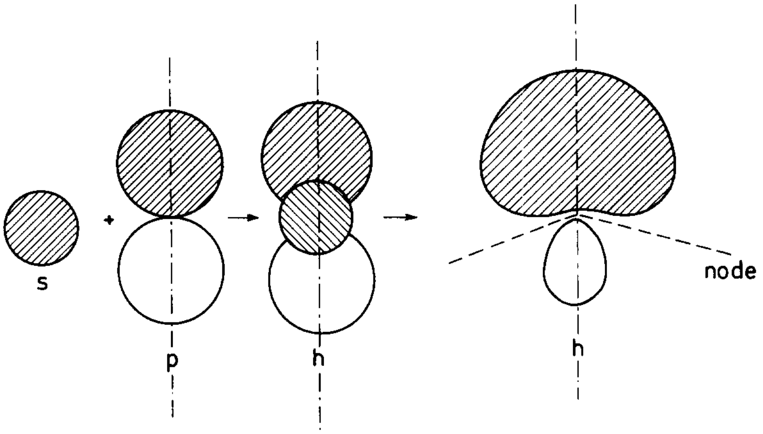

Fig. 4. Formation of a hybrid by superposition of one *s*- and one *p*-type orbital.

utilizing the maximum overlapping principle in addition to the symmetry arguments. This holds quite generally because symmetry yields only qualitative information about systems under study. Its strength, however, can be considerably enhanced by using additional criteria dictated by the physics of the situation. The simple interpretation of the shapes of $H_2S$, $H_2Se$ and $H_2Te$ is attractive, but it has limitations. For example, the bond angle in the $H_2O$ molecule is 104.5°, indicating that other effects are also of importance. However, they have nothing to do with symmetry and concomitantly will not be discussed here.

Stereochemistry of the carbon atom requires a new concept. Its electron configuration $(1s)^2(2s)^2(2p)^2$ suggests that carbon is divalent. In spite of the fact that unusual molecules like $CH_2$ and $CF_2$ do exist, the whole of organic chemistry rests on the tetravalency of carbon atoms. The latter is most easily explained by the promotion of one electron from the $2s$ level to the empty $2p$ orbital. Thus, the so-obtained four uncoupled spins are responsible for the carbon quadrivalency. They do not yield desired directional characteristics, though, because the configuration $(1s)^2(2s)(2p_X)(2p_Y)(2p_Z)$ involves only three orbitals projected into $X$, $Y$ and $Z$ directions. The $CH_4$ molecule, on the other hand, has beautiful tetrahedral structure. The problem was elegantly solved by Pauling[29] and somewhat later by Slater[30]. They introduced hybrid-orbital linear combinations of free-atom eigenfunctions

$$h_i = c_{i1}(2s) + c_{i2}(2p_X) + c_{i3}(2p_Y) + c_{i4}(2p_Z). \tag{4}$$

Hence by sacrificing the angular momentum quantum number $l$, it is possible to construct four equivalent orthonormal hybrids of the form (4), which are directed toward the corners of a tetrahedron. Furthermore, these hybrid orbitals have the axial symmetry required for the description of four local $\sigma$-bonds. They have a number of favourable properties. First, hybrids have a characteristic mushroom-like form (Fig. 4), which is a consequence of the reinforcement of the $s$ and $p$ orbitals in the domain of their positive signs, and destructive interference and partial cancellation of the $s$ and $p$ amplitudes in the region of their opposite signs. Hence, the hybrid orbital is strongly polarized toward its nearest neighbour. It was shown by Pauling that tetrahedral hybrids not only have proper directional features but also considerable bond strength, which overcompensates the price in energy paid by the $s$–$p$ promotion[29]. Finally, by maximizing the overlapping power in one particular direction the hybrid's amplitudes are minimized in all others. Consequently, the nonbonded repulsions are usually minimized at the same time.

It is easy to see that symmetry operations of the $T_d$ point group transform tetrahedral orbitals between themselves. Therefore, they form a basis for the representation of the $T_d$ group. This representation is reducible because it is four dimensional, while the highest dimension of the irreducible representations of the $T_d$ group is 3 (Table 3). Two points of importance will be considered here: (a) selection of the AOs of the central atom suitable for the construction of the general hybrid orbitals belonging to the $T_d$ symmetry and (b) determination of the coefficients $c_{ij}$(4) by group-theoretical arguments. For this purpose we shall make use of group represen-

Table 3. Characters of the (ir)reducible representations of the $T_d$ group and the corresponding basis functions

| $T_d$ | $I$ | $8C_3$ | $3C_2$ | $6S_4$ | $6\sigma_d$ | Basis sets |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 | $s$, $f_{XYZ}$ |
| $A_2$ | 1 | 1 | 1 | −1 | −1 | |
| $E$ | 2 | −1 | 2 | 0 | 0 | $(d_{Z^2}, d_{X^2-Y^2})$ |
| $T_1$ | 3 | 0 | −1 | 1 | −1 | $(f_{X(z^2-y^2)}, f_{Y(z^2-x^2)}, f_{Z(x^2-y^2)})$ |
| $T_2$ | 3 | 0 | −1 | −1 | 1 | $(p_X, p_Y, p_Z)(d_{XY}, d_{XZ}, d_{YZ})(f_{x^3}, f_{y^3}, f_{z^3})$ |
| $\Gamma_h$ | 4 | 1 | 0 | 0 | 2 | $(h_1, h_2, h_3, h_4)$ |

tations. The characters of the reducible representation $\Gamma_h$ generated by four equivalent tetrahedral hybrids are easily obtained by inspection. They are simply equal to the numbers of the hybrid AOs which retain their positions after the symmetry operation was performed. The permutations of hybrids by symmetry operations are easily examined with the aid of Fig. 5, where the hybrids $h_i$ directed to the hydrogens $H_i$ are represented by arrows. Knowing the character of the $\Gamma_h$ representation (Table 3), its irreducible components are found by employing the great orthogonality theorem[60]. The result reads

$$\Gamma_h = A_1 \oplus T_2. \tag{5}$$

Hence, the hybrid orbitals can be composed of AOs which belong to $A_1$ and $T_2$ irreducible representations, respectively. The spherical harmonics of the given $l$ span the $2l + 1$ dimensional irreducible representation of the group of three-dimensional rotations $K_h$. They are generally split by the descent of symmetry $K_h \rightarrow T_d$. A simple way to examine the behaviour of the spherical harmonics in the molecular field of the $T_d$ symmetry is to take their Cartesian representation (Table 2) and execute the required coordinate transformation corresponding to the $I$, $C_3$, $C_2$, $S_4$ and $\sigma_d$ symmetry operations[60,61]. One finds out that the $p$ subshell remains degenerate while $d$ and $f$ subshells are split into two and three levels, respectively (Table 3). It appears that functions $s$ and $f_{XYZ}$ belong to the irreducible representation $A_1$. On the other hand, three sets of the three independent functions $(p_X, p_Y, p_Z)$, $(d_{XY}, d_{XZ}, d_{YZ})$ and $(f_{X^3}, f_{Y^3}, f_{Z^3})$ span the irreducible representation $T_2$. Obviously, the hybridization scheme is not unique and several combinations of AOs which belong to $A_1$ and $T_2$ representations are possible. One can combine one $s$ orbital and three $p_X$, $p_Y$ and $p_Z$ orbitals to form the most conventional $sp^3$ tetrahedral hybrids. Alternatively, the $sd^3$, $sf^3$, $fd^3$ and $f^4$ schemes may take place or any combinations thereof. We shall postpone their discussion for the moment, in order to obtain

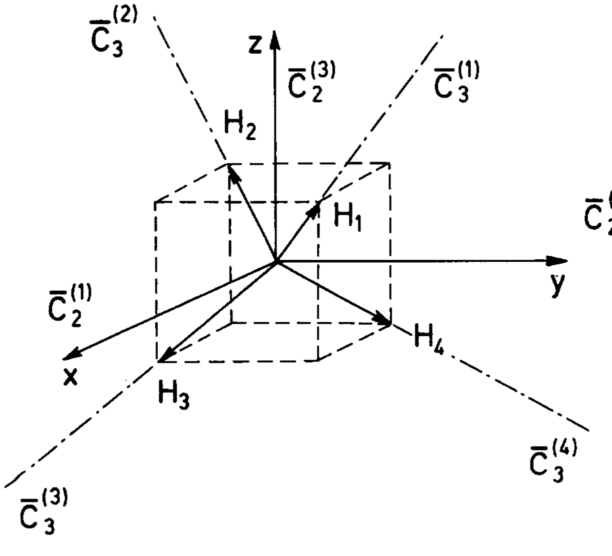

Fig. 5. Tetrahedral directions and some symmetry elements of the $T_d$ point group.

explicit form of the $sp^3$ hybrids $h_i(4)$. This can be achieved by using a very practical device called projection operator[60,61]:

$$\hat{P}_\mu = \sum_R \chi_\mu(R)^* \hat{O}_R, \tag{6}$$

where $\chi_\mu(R)$ is the character of the $\mu$th irreducible representation corresponding to the symmetry operation $R$ and the summation is extended over all symmetry operations of the point group in question. The operator denoted by $\hat{O}_R$ is associated with the transformation of the basis set functions induced by the symmetry operator $\hat{R}$ and defined by

$$\hat{O}_R f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r}). \tag{7}$$

The operator $\hat{P}_\mu$ has a property that when applied to an arbitrary function, the component of that function belonging to the $\mu$th irreducible representation is projected out while the rest of it is abolished. The effect of the $\hat{O}_R$ operators on the tetrahedral hybrids $h_i$ are summarized in Table 4. We can arbitrarily single out the $h_1$ hybrid and apply the $\hat{P}_{A_1}$ operator to extract the $A_1$ contribution of the hybrid. Straightforward application of the formula (6) and the data given in Table 4 yields

$$\hat{P}_{A_1} h_1 = 6(h_1 + h_2 + h_3 + h_4). \tag{8}$$

Since the hybrids $h_i$ are orthogonal by assumption, the normalized form of $\hat{P}_{A_1} h_1$ should be equal to the $s$ orbital which will be used for hybridization. Hence

$$(h_1 + h_2 + h_3 + h_4)/2 = s. \tag{9}$$

Analogously, $\hat{P}_{T_2}$ operator applied to $h_1$, $h_2$ and $h_3$ hybrids gives after normalization three linearly independent functions belonging to the $T_2$ irreducible representation. They are generally equal

Table 4. Transformation of the $T_d$ hybrids under $\hat{O}_R$ for all symmetry operations $R$ of the $T_d$ group

| $h_i$<br>$R$ | $h_1$ | $h_2$ | $h_3$ | $h_4$ |
|---|---|---|---|---|
| $I$ | $h_1$ | $h_2$ | $h_3$ | $h_4$ |
| $C_3^{(1)}$ | $h_1$ | $h_4$ | $h_2$ | $h_3$ |
| $(C_3^{(1)})^2$ | $h_1$ | $h_3$ | $h_4$ | $h_2$ |
| $C_3^{(2)}$ | $h_3$ | $h_2$ | $h_4$ | $h_1$ |
| $(C_3^{(2)})^2$ | $h_4$ | $h_2$ | $h_1$ | $h_3$ |
| $C_3^{(3)}$ | $h_4$ | $h_1$ | $h_3$ | $h_2$ |
| $(C_3^{(3)})^2$ | $h_2$ | $h_4$ | $h_3$ | $h_1$ |
| $C_3^{(4)}$ | $h_2$ | $h_3$ | $h_1$ | $h_4$ |
| $(C_3^{(4)})^2$ | $h_3$ | $h_1$ | $h_3$ | $h_4$ |
| $C_2^{(1)}$ | $h_3$ | $h_4$ | $h_1$ | $h_2$ |
| $C_2^{(2)}$ | $h_4$ | $h_3$ | $h_2$ | $h_1$ |
| $C_2^{(3)}$ | $h_2$ | $h_1$ | $h_4$ | $h_3$ |
| $S_4^{(1)}$ | $h_4$ | $h_1$ | $h_2$ | $h_3$ |
| $(S_4^{(1)})^3$ | $h_2$ | $h_3$ | $h_4$ | $h_1$ |
| $S_4^{(2)}$ | $h_2$ | $h_4$ | $h_1$ | $h_3$ |
| $(S_4^{(2)})^3$ | $h_3$ | $h_1$ | $h_4$ | $h_2$ |
| $S_4^{(3)}$ | $h_3$ | $h_4$ | $h_2$ | $h_1$ |
| $(S_4^{(3)})^3$ | $h_4$ | $h_3$ | $h_1$ | $h_2$ |
| $\sigma_d^{(1)}$ | $h_1$ | $h_2$ | $h_4$ | $h_3$ |
| $\sigma_d^{(2)}$ | $h_1$ | $h_4$ | $h_3$ | $h_2$ |
| $\sigma_d^{(3)}$ | $h_1$ | $h_3$ | $h_2$ | $h_4$ |
| $\sigma_d^{(4)}$ | $h_4$ | $h_2$ | $h_3$ | $h_1$ |
| $\sigma_d^{(5)}$ | $h_3$ | $h_2$ | $h_1$ | $h_4$ |
| $\sigma_d^{(6)}$ | $h_2$ | $h_1$ | $h_3$ | $h_4$ |

to some orthonormalized linear combinations of the $p_X$, $p_Y$ and $p_Z$ AOs:

$$\hat{P}_{T_2}h_1 \sim (3h_1 - h_2 - h_3 - h_4)/\sqrt{12}$$
$$= \pm(a_{11}p_X + a_{12}p_Y + a_{13}p_Z)/(a_{11}^2 + a_{12}^2 + a_{13}^2)^{1/2}, \quad (10a)$$

$$\hat{P}_{T_2}h_2 \sim (-h_1 + 3h_2 - h_3 - h_4)/\sqrt{12}$$
$$= \pm(a_{21}p_X + a_{22}p_Y + a_{23}p_Z)/(a_{21}^2 + a_{22}^2 + a_{23}^2)^{1/2}, \quad (10b)$$

$$\hat{P}_{T_2}h_3 \sim (-h_1 - h_2 + 3h_3 - h_4)/\sqrt{12}$$
$$= \pm(a_{31}p_X + a_{32}p_Y + a_{33}p_Z)/(a_{31}^2 + a_{32}^2 + a_{33}^2)^{1/2}. \quad (10c)$$

Applying the operator $\hat{O}_{C_3^{(1)}}$ to eqn (10a) one obtains

$$(3h_1 - h_2 - h_3 - h_4)/\sqrt{12} = \pm(p_X + p_Y + p_Z)/\sqrt{3}, \quad (11)$$

which follows from the fact that the left side is invariant and

$$\hat{O}_{C_3^{(1)}}p_X = p_Z, \quad \hat{O}_{C_3^{(1)}}p_Y = p_X, \quad \hat{O}_{C_3^{(1)}}p_Z = p_Y.$$

Consequently, $a_{11} = a_{13}$, $a_{12} = a_{11}$, $a_{12} = a_{13}$, and the only dilemma left is the sign of the right-hand side in (11). Taking into account that $p_X$, $p_Y$ and $p_Z$ AOs behave like components of the position vector, the linear combination $(p_X + p_Y + p_Z)/\sqrt{3}$ is colinear with the $h_1$. Hence, the positive sign is appropriate:

$$(3h_1 - h_2 - h_3 - h_4)/\sqrt{12} = (p_X + p_Y + p_Z)/\sqrt{3}. \quad (12a)$$

Similarly, by acting with $\hat{O}_{C_3^{(2)}}$ and $\hat{O}_{C_3^{(3)}}$ operators on eqns (10b) and (10c), respectively, one readily obtains

$$(-h_1 + 3h_2 - h_3 - h_4)/\sqrt{12} = -(p_X + p_Y - p_Z)/\sqrt{3} \quad (12b)$$

and

$$(-h_1 - h_2 + 3h_3 - h_4)/\sqrt{12} = (p_X - p_Y - p_Z)/\sqrt{3}. \quad (12c)$$

Simple algebra shows that the system of eqns (12a–c) can be transformed to an equivalent form:

$$\begin{aligned} p_X &= (h_1 - h_2 + h_3 - h_4)/2, \\ p_Y &= (h_1 - h_2 - h_3 + h_4)/2, \\ p_Z &= (h_1 + h_2 - h_3 - h_4)/2. \end{aligned} \quad (13)$$

Equations (9) and (13) can be succintly written as

$$\begin{Vmatrix} s \\ p_X \\ p_Y \\ p_Z \end{Vmatrix} = \frac{1}{2} \begin{Vmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \end{Vmatrix} \cdot \begin{Vmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \end{Vmatrix}. \quad (14)$$

The inverse matrix transformation would yield the desired composition of the hybrids $h_i (i = 1, \ldots, 4)$ in terms of $s$, $p_X$, $p_Y$ and $p_Z$ AOs. Noting that the two orthogonal basis sets (14) are related by the orthogonal matrix, one immediately obtains

$$\begin{Vmatrix} h_1 \\ h_2 \\ h_3 \\ h_4 \end{Vmatrix} = \frac{1}{2} \begin{Vmatrix} 1 & 1 & 1 & 1 \\ 1 & -1 & -1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \end{Vmatrix} \cdot \begin{Vmatrix} s \\ p_X \\ p_Y \\ p_Z \end{Vmatrix}. \tag{15}$$

Thus the explicit form of the $sp^3$ hybrids (4) reads

$$\begin{aligned} h_1 &= (s + p_X + p_Y + p_Z)/2, \\ h_2 &= (s - p_X - p_Y + p_Z)/2, \\ h_3 &= (s + p_X - p_Y - p_Z)/2, \\ h_4 &= (s - p_X + p_Y - p_Z)/2. \end{aligned} \tag{16}$$

Let us focus attention to the alternative $sd^3$ and $sf^3$ hybridization schemes. The crucial point of the procedure above was the behaviour of the $p_X$, $p_Y$ and $p_Z$ AOs under the action of the $\hat{O}_{C_3^{(i)}}$ ($i = 1, 2, 3$) operators. It can be easily shown that the vectors

$$\begin{Vmatrix} p_X \\ p_Y \\ p_Z \end{Vmatrix}, \quad \begin{Vmatrix} d_{YZ} \\ d_{XZ} \\ d_{XY} \end{Vmatrix} \quad \text{and} \quad \begin{Vmatrix} f_{X^3} \\ f_{Y^3} \\ f_{Z^3} \end{Vmatrix}$$

have the same transformation properties when the $\hat{O}_{C_3^{(1)}}$, $\hat{O}_{C_3^{(2)}}$ and $\hat{O}_{C_3^{(3)}}$ are applied. Hence, the $sd^3$ and $sf^3$ hybrids are straightforwardly obtained from eqns (16) by substitutions based on formal equivalence:

$$\begin{aligned} p_X &\longleftrightarrow d_{YZ} \longleftrightarrow f_{X^3}, \\ p_Y &\longleftrightarrow d_{XZ} \longleftrightarrow f_{Y^3}, \\ p_Z &\longleftrightarrow d_{XY} \longleftrightarrow f_{Z^3}. \end{aligned} \tag{17}$$

The $sp^3$, $sd^3$, $sf^3$ and the earlier-mentioned tetrahedral hybridization compositions like $fp^3$, $fd^3$ and $f^4$ are all equivalent from the point of view of group theory. Apparently, some more physical insight is needed here to determine the optimal hybridization. Consider the $sd^3$ scheme for the C atom. Radial parts of the AOs were tacitly assumed to be independent on the quantum number $l$ so far. The matter of truth is that the chain of inequalities for the effective nuclear charge

$$Z_s > Z_p > Z_d > Z_f$$

usually holds, implying that

$$E_s < E_p < E_d < E_f.$$

To be more specific, the $2p$ level lies by some 207 kcal/mole above the $2s$ level. The $3d$ level is about 230 kcal/mole less stable than the $2p$ level, etc. Therefore, it is obvious that the $sp^3$ scheme is much more important in describing the charge distribution of the tetracoordinate carbon atom than the $sd^3$ one. Another difference is given by the number of angular nodes of $p$ and $d$ orbitals. The $d_{Z^2}$ orbital (Fig. 2) has two positive lobes along the $Z$ axis and mixing in a certain amount of the $s$ orbital will reinforce the hybrid in two diametraly opposite directions. Hence, $sd_{Z^2}$ will be less polarized toward a specific neighbour than the $sp_Z$ hybrid. Magnitudes of the corresponding overlap integrals clearly show that the latter is more favourable. It is also easy to see that the $f_{Z^3}$ orbital behaves like the $p_Z$ orbital as far as the $Z$ axis is concerned. The $sf_{Z^3}$ hybrid, however, has less efficient overlapping power. Nonetheless, it is plausible to assume that an optimal hybrid will have some admixture of $d$ and $f$ orbitals. Indeed, a small amount of the $d$ orbital would be beneficial. The $sp^3$ hybrid has a small negative lobe which can be further diminished by the contribution of the properly oriented $d$ orbital. The large positive lobe is enhanced at the same time. Neglecting the influence of the $f_{XYZ}$ orbital, which belongs to the $A_1$ irreducible representation like the $s$ orbital but is obviously less effective, we conclude that the general hybrid of the tetrahedral symmetry takes a form

$$h_1 = a(2s) + b(2p_X + 2p_Y + 2p_Z) + c(3d_{YZ} + 3d_{XZ} + 3d_{XY}) + d(4f_{X^3} + 4f_{Y^3} + 4f_{Z^3}). \quad (18)$$

The coefficients in formula (18) cannot be estimated by group theory. The most accurate procedure would be the use of the variation theorem. However, some idea about the magnitude of the coefficients could be obtained by the simple bond strength criterion. According to Pauling, the optimal hybrid is the one with the maximum angular amplitude in the bond direction[29]. Taking into account the promotion energies, Pauling[62] found that the hybrid

$$h_1 = 0.50(2s) + 0.83(2p_Z) + 0.20(3d_{Z^2}) + 0.14(4f_{Z^3}) \quad (19)$$

has a pronounced bonding power. Hence, the contributions of the $d_{Z^2}$ and $f_{Z^3}$ AOs of 4% and 2%, respectively, are small but significant. Generally speaking, the efficiency in the mixing of AOs depends very much on their sizes, which should be taken into account in the semiquantitative calculations.

The hybridization of the trigonal (ethylene) and digonal (acetylene) carbon atoms can be analyzed along the same lines. It should be pointed out in this respect that the widely used $sp^2$ and $sp^1$ canonical hybridization schemes are more exception than rule (*vide infra*). Two approaches are possible in the treatment of multiple bonding: (a) $\sigma$–$\pi$ separation of orbitals which in turn differ in symmetry characteristics relative to the bond axis and (b) deformed tetrahedron picture, which leads to the bent-bond representation of the multiple bonding. These two approaches differ in the choice of the basis set. They are equivalent in the MO theory if the calculations are pursued far enough. However, the bent-bond picture is to be preferred in the VB method if the calculation involves only the most important valence structures, particularly if $d$ and $f$ AOs are employed[62].

The hybridization is most effective in carbon atoms. This is not surprising because the loss in energy by the $2s$–$2p$ promotion is highly rewarded by the formation of the two additional covalent bonds. This is not the case, for example, in oxygen and nitrogen, where the increase in $s$ character of hybrids improves overlapping, but does not yield new bonds. Hence, the role of hybridization is less pronounced in this type of atom. Concomitantly, the hybridization in atoms other than carbon was less extensively studied. It should be noted that the general $s^kp^ld^m$ hybridization schemes were investigated by Kimball[63,64] and were extended later to $s^kp^ld^mf^n$ phenotypes by the group-theoretical study of Eisenstein[65]. It is also noteworthy that hybridization of the central atom suitable for the $\pi$-bonding with appropriate ligand AOs can be determined on the same footing[60,61]. The most relevant hybrids for inorganic compounds are described in Pauling's classical book *The Nature of the Chemical Bond*[62]. This armamentarium was considerably enlarged by a series of papers based on the maximum of bond strength criterion which appeared over the last ten years[34,36,37,39,41,43,53,54]. Some recent advances were discussed in depth by Herman[52].

## HYBRIDIZATION AND MOLECULAR PROPERTIES

The charge distribution of an atom in a molecule is anisotropic. Consequently, it is advantageous to use some sort of chemically adapted AOs, which conform themselves to the local site symmetry dictated by the immediate environment, if a simple and economical description of molecular properties is desired. This type of AO provides hybridization. Hence, hybrids can be considered as local wavefunctions of the zeroth order. It follows as a corollary that hybrids are very helpful in rationalizing those molecular properties which can be ascribed to chemical bonds. This is indeed the case[47,51,52,62,66], as shall be seen shortly.

### *Molecular shape and size*

Hybrid orbitals were designed to explain directional properties of homopolar bonds. Therefore, they should give some insight into the bond angles in molecules. In spite of the fact that hybrids do not always coincide with straight lines passing through the neighbouring nuclei, they do give some useful information about bond angles and regularities in their changes. This is based on the intimate relation between the hybrid composition and the interhybrid angle $\vartheta$. Consider for simplicity two equivalent and orthogonal $sp^n$ hybrids:

$$h_i = a_i(2s) + (1 - a_i^2)^{1/2}(2p)_i \quad (i = 1, 2), \tag{20}$$

where $(2p)_i$ is the properly oriented $p$ orbital $(2p)_i = \cos\gamma_X(2p)_X + \cos\gamma_Y(2p)_Y + \cos\gamma_Z(2p)_Z$ and $\cos\gamma_\alpha(\alpha = X, Y, Z)$ are the direction cosines. The orthogonality requirement yields

$$\cos\vartheta_{12} = -1/n_i \quad (i = 1, 2), \tag{21}$$

where the hybridization parameter $n_i = (1 - a_i^2)/a_i^2$ is by definition a positive number. It gives a ratio between the $p$ and $s$ populations in the hybrid. Hence, it immediately follows that two equivalent hybrids can form an angle which must be larger than 90°, which leads to bent bonds in small rings. Furthermore, the orthogonality condition yields for the $C_{2v}$ local symmetry case a relation

$$\cos\vartheta_{34} = (\cos\vartheta_{12} + 1)/(3\cos\vartheta_{12} - 1), \tag{22}$$

$\vartheta_{34}$ denoting the angle between the second pair of the hybrids placed on the same nucleus. It is easy to see that an increase in one angle is accompanied by a decrease in the other. This is empirically known as the Thorpe–Ingold effect[67]. Therefore, a functional relationship between the two structurally independent parameters [(22)] is established through the hybridization concept. It should be kept in mind that the relation (22) leans rather heavily on the orthogonality requirement, which is plausible but by no means necessary, because hybrid AOs are not atomic eigenfunctions. Nevertheless, it is expected that overlapping of the single-center hybrids is very low because the electrons usually assume a state of the maximum spin multiplicity according to Hund's rule. Hence their spatial wavefunctions will try to avoid each other as much as possible to satisfy the Pauli principle. Even if the electron spins are random, the overlapping should be small because the valencies would otherwise be internally saturated. On the other hand, one can suppose on intuitive grounds that hybrids emanating from the same atom are orthogonal (or nearly so) because the interaction between bonds should be at a minimum if their individuality is to be retained. A concept of a localized covalent bond, on the other hand, is a well-founded empirical fact. Study of the hybridization by the semiempirical MO methods showed that the deviations from orthogonality are small for carbon atoms[68]. Relation (22) holds, of course, only approximately due to the neglect of higher AOs, steric effects, etc.[69,70]. It explains nicely, however, the opening up of the bond angle in $CH_2$ groups attached to small carbocycles[71,72]. The same feature exhibits the $SiH_2$ group in silacarbocycles[73]. This is easily explained by the increase in $s$ content of the C—H (or Si—H) hybrids caused by the concomitant increase of the $p$ character in hybrids describing a small ring. This rehybridization is a consequence of the tendency of the molecule to reduce the angular strain. The opposite is the case of the $CH_2$ group in the ethylene moiety. A multiple bond is always stronger in competing for the $s$ character. Therefore, the HCH angle decreases to 117.5°[71], which is an experimental fact. It should be mentioned that in these calculations[71–73] the maximum overlap criterion is employed for the prediction of interhybrid angles. This approach also gives fair estimates of dihedral angles in polycyclic systems and explains puckering of some six-, seven-, and eight-membered carbocycles[74,75]. Pauling's maximum hybrid orbital strength model is simple and attractive because it is free of parametrization. It gives purely theoretical estimates of bond angles. Stereochemistry is determined in this model exclusively by the central atom. This is a strong point because it gives conclusions which are perfectly general. The weakness, however, is complete neglect of the ligand influence. The model was applied to interpret and predict the structural properties of inorganic compounds, particularly transition-metal complexes[34,36,37,41,43,53,76–78] employing *spd* and *spdf* basis sets. The fundamental importance of enneacovalence (nine covalent bonds) in determining structures of transition-metal compounds was revealed. Analysis of the $sp^3d^5$ hybrids has led to some remarkable conclusions: (a) there are two nodal cones of an $sp^3d^5$ hybrid which make angles of 73.2° and 133.6°, respectively, with the hybrid orbital axis. These angles determine domains in space where other hybrids can take place. It appears that the nodal cone is exactly the direction in which the other hybrid(s) assume the maximum bonding strength. (b) Two optimal polyhedra for enneacovalent transition metal atoms were determined. They correspond to hybrids with maximum bonding power and have the following forms: (1) trigonal prism with equatorial caps on the three rectangular faces and (2) tetragonal antiprism with a polar cap on one of the two bases. These polyhedra seem to play the same crucial role in transition-metal chemistry as the tetrahedron in organic chemistry. Furthermore, the best bonding set of eight $sp^3d^4$ hybrids form either a Archimedean (square) antiprism or a tetragonal dodecahedron. A large number of transition-metal structures was analysed along these lines and reasonable agreement with the experimental data, when available, was obtained. Admixtures of $f$ and $g$ orbitals in describing bonding in transition-metal clusters was discussed[39]. Finally, optimal hybrid AOs for pentacovalent bonding situations were described[54].

Hybridization not only gives reasonable descriptions of molecular shapes, but also provides fair estimates of their sizes. Results of the iterative maximum overlap (IMO) method[71,75] should be emphasized. The underlying idea that bond radius directly depends on the hybrid's composition was pointed out first by Coulson[79]. Additionally, Dewar and Schmeising have shown that CC and CH bond lengths can be classified according to canonical hybridization states of the constituent carbon atoms[80]. This has been generalized in the IMO approach by including more flexible $sp^n$ ($n$ is any real number) hybrids within the framework of the IMO approach and good estimates of the structural characteristics of hydrocarbons were obtained. They can be favourably compared with the data obtained by much more intricate computations[72]. The IMO method seems to enjoy a remarkable predictive value. For example, the shortening of the interatomic distances belonging to central rings in rotanes was predicted on the basis of the IMO calculations[81]. This was subsequently confirmed by experimental measurements[82]. The estimated structure of the parent tetrahedrane[71a] (not yet synthetized) seems to be essentially correct[71b]. A compression of the double bonds emanating from small rings due to the redistribution of the $s$ characters is predicted[83,84]. The structural properties of the disiloxy group and its derivatives were recently interpreted by hybrid orbitals distilled from *ab initio* wavefunctions[85]. The relevance of the hybridization concept in rationalizing molecular structures was recently discussed by Allen *et al.*[86]. To conclude, hybridization provides relations not only between the bond angles themselves but also serves as a guide in interpreting a number of relationships which do exist between bond lengths and angles.

### *Charge density distributions*

Electron isopycnic (isodensity) maps reflect the changes in charge distributions accompanying the formation of molecules[87,88]. Particularly informative for this purpose are deformation density contours. They are defined as a difference between the total molecular electron density and the superposition of atomic densities obtained by placing neutral atoms on the equilibrium positions and setting all their interactions equal to zero. This ensemble of atoms is called a promolecule. Its density distribution can be found only by accurate *ab initio* calculations. Hence, strictly speaking the deformation density maps are not observable. Nevertheless, they visualize the changes caused by bonding interactions in a very transparent way. One observes as a rule humps of the electron density in the region between the bonded atoms if they have moderate electronegativities. There is usually a depletion of charge in the rest of the molecules, particularly in their peripheral parts. Two important points should be stressed: (a) The changes in density are small as compared with the total molecular density, thus supporting the idea of perturbed atoms; (b) humps of the density nicely reflect a decrease in symmetry and distortion of atoms in chemical environments. This is exemplified by the X-ray deformation density map

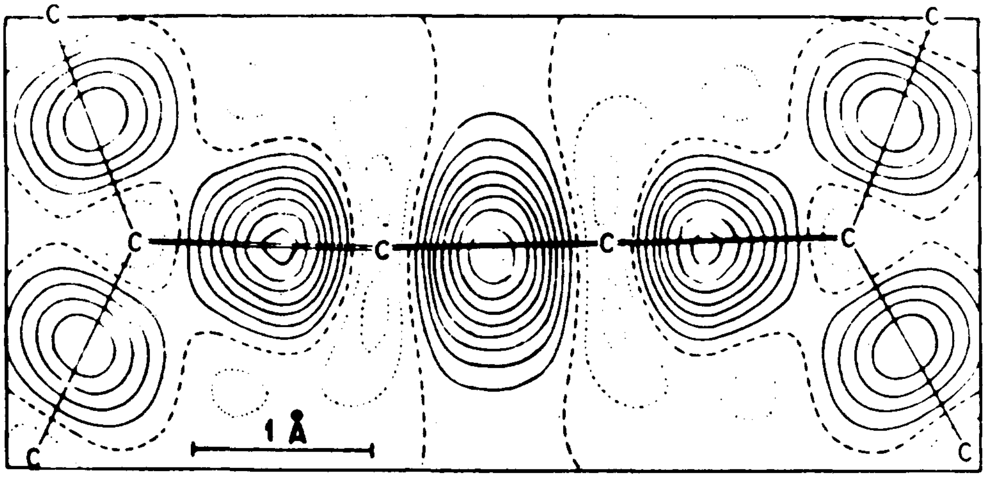

Fig. 6. Deformation density contours in butatriene part of the tetraphenylbutatriene.

taken in the butatriene plane of the tetraphenyl-substituted derivative (Fig. 6). One can notice distributions which are characteristic for $sp^2$ and $sp^1$ phenotypes of hybridization. The depicted map does not prove the "existence" of hybrids in this and other molecules, because for one thing the hybrid AOs are one-electron wavefunctions. Consequently, they are no more and no less real than the other atomic orbitals, the hydrogen wavefunction being an exception since it is a true solution. Figure 6 does show, however, that hybrid AOs are well adapted for a description of the atomic charge anisotropy.

A completely new feature is found in small strained rings. Theoretical isopycnic and deformation density maps based on local hybrid AOs exhibit considerable shift of the bond density off the geometric straight line joining the neighbouring carbon atoms[90]. Therefore the well-known bent bonds appear, discussed first in cyclopropane by Förster[91] and elaborated on later by Coulson and Moffitt in their famous paper[92]. It is interesting to mention that bent bonds were theoretically predicted some 25 years before they were experimentally found by X-ray measurements[87]. There are also numerous *ab initio* studies of strained systems by this point[93]. A number of unusual properties of small cyclic and polycyclic compounds can be rationalized in terms of bent bonds, to mention only Baeyer angular strain and pronounced chemical reactivity, for example. A bent chemical bond is not axially symmetric any more. It provides another example which shows that new facets can be expected if the symmetry is destroyed.

### *Energetic properties and hybridization*

The relation between the directional properties of bonds and the total molecular energy is something which can be anticipated. If the postulate of the chemical bond formed by a localized pair of electrons is adopted, then it is plausible to assume that their spatial distributions will minimize the interbond repulsion, leading to the stable geometrical structure. The position of a hybrid and its direction in space depend on its $s$, $p$, etc. composition, but so does its bonding power and overlapping ability. This yields an additional link between the energy and directional features. It is difficult to delineate bonding and nonbonding effects because they are strongly interlocked. However, the former prevail at any rate since molecules are stable species. Therefore we shall focus our attention on stabilizing interactions. As mentioned earlier, the maximum hybrid strength yields a qualitative index of bond energies[62]. Good estimates of instantaneous bond dissociation energies (IBDE) in hydrocarbons were obtained by scaling the corresponding bond overlaps[94]. The former were defined as the energies necessary to break the bond, leaving the formed fragment radicals unrelaxed. A sum of weighted bond overlap integrals was correlated with the observed enthalpies of formation $\Delta H_f$, supposing that the bond energy follows an additivity scheme. Quite reasonable results were obtained for a variety of hydrocarbons[95]. They are reliable enough to predict $\Delta H_f$ values in unknown compounds and to offer useful estimates of the heats of hydrogenation $\Delta H_h$[95]. By reversing the argument, one can say that hybridization and its characteristic transferability between similar molecular fragments gives the simplest explanation of the $\Delta H_f$ additivity. The angular strain caused by deformed electron densities can be related to hybrid bending and a concomitant defect in overlapping[95].

*Spin–spin coupling constants across a bond*

Indirect coupling of spins of the directly bonded nuclei takes place via the coupled electron pair. Hence the interpretation by localized MOs seems to be an obvious choice. The situation is not simple, however, because the coupling constant is a sum of several terms[96]. Fortunately, the Fermi contact term (FC) is a dominant effect in hydrocarbons and thus can be singled out as the most important contribution. Since the FC term depends on the extent of electron penetration into the nuclei, a direct connection with $s$ characters of the corresponding hybrids follows:

$$J(\mathrm{AB}) = k_{\mathrm{AB}}c_{\mathrm{A}}^2c_{\mathrm{B}}^2 + l_{\mathrm{AB}}, \tag{23}$$

where A and B stands for C and H atoms, $c_{\mathrm{A}}^2$ and $c_{\mathrm{B}}^2$ are $s$-orbital populations of the hybrids, and the optimal empirical parameters are denoted by $k_{\mathrm{AB}}$ and $l_{\mathrm{AB}}$. Relation (23) is of course an approximate one. It involves the well-known Muller–Pritchard (A═C, B═H) and the Frei–Bernstein (A═C, B═C) formulas if the adjusting factors $k_{\mathrm{AB}}$ and $l_{\mathrm{AB}}$ assume the prescribed values[96]. The average excitation energy $\Delta E$ appearing in the denominator of the first term was included in the $k_{\mathrm{AB}}$ parameter. Furthermore, the normalization constant of the VB function describing the AB fragment is neglected here. Its inclusion gives slight quantitative improvement[97] but it is not essential for our purpose here. Extensive semiempirical calculations have conclusively shown that relation (23) holds to a reasonable degree of accuracy[96–98]. Some care has to be exercised when multiple bonds are involved because non-Fermi terms cannot be omitted anymore[96,99]. Nevertheless, despite some reservations[100], it is beyond doubt now that $J$(CC) and $J$(CH) couplings are intimately related to hybridization states of the carbon atoms in question. If this is accepted, then the empirically observed relations between the $J$(CH) coupling constants, $d$(C—H) bond distances[101] and C—C—C bond angles in cyclic compounds[102] become perfectly understandable. The same conclusion holds for the connection between $J$(C—H) and $J$(CC) couplings involving the common carbon atom[103]. Furthermore, a linear relation between the $\nu$(C—H) stretching frequencies and $J$(C—H) spin–spin couplings was proposed on theoretical grounds[104]. Finally, the experimental CC stretching force constants were linearly related to the corresponding $J$(CC) coupling constants[105]. Needless to say, the unifying concept underlying all these interrelations between different observables is hybridization.

*Photoelectron spectroscopy and hybridization*

Photoelectron spectroscopy (PES) is a playground for the MO theory. Simple MO schemes are usually very effective in interpreting PES spectra and provide useful aids in their assignments[106]. Hybrid orbitals seem to be inappropriate for this purpose at first glance. However, this is not always the case. We shall discuss it in some more detail because the symmetry arguments are particularly useful in this respect. Consider, for example, the $CH_4$ molecule. The molecular orbitals can be constructed consecutively by forming first the localized two-center orbitals:

$$\lambda_i = \frac{1}{\sqrt{2}}(h_i + H_i), \tag{24}$$

where $h_i$ are $sp^3$ hybrids (16) and $H_i$ stands for the $1s_{H_i}$ hydrogen functions. It is tacitly assumed that the C—H bonds are purely covalent and the overlap is neglected in the normalization constant for simplicity. The delocalized MOs of $A_1$ and $T_2$ symmetry species are readily produced by using projection operator (6) technique (*vide supra*). They read as follows:

$$A_1{:}\quad \psi_1 = \frac{1}{2\sqrt{2}}[(h_1 + h_2 + h_3 + h_4) + (H_1 + H_2 + H_3 + H_4)], \tag{25a}$$

$$\psi_2' = \frac{1}{2\sqrt{6}}[(3h_1 - h_2 - h_3 - h_4) + (3H_1 - H_2 - H_3 - H_4)]; \tag{25b}$$

$$T_2: \quad \psi_3' = \frac{1}{2\sqrt{6}}[(-h_1 + 3h_2 - h_3 - h_4) + (-H_1 + 3H_2 - H_3 - H_4)], \tag{25c}$$

$$\psi_4' = \frac{1}{2\sqrt{6}}[(-h_1 - h_2 + 3h_3 - h_4) + (-H_1 - H_2 + 3H_3 - H_4)]. \tag{25d}$$

By using formula (9) one straightforwardly obtains

$$\psi_1 = \frac{1}{\sqrt{2}}\left[s + \frac{1}{2}(H_1 + H_2 + H_3 + H_4)\right]. \tag{26a}$$

One can take advantage of the fact that the molecular orbitals belonging to the $T_2$ irreducible representation are degenerate. They can therefore be combined to simplify the formulas (25b–d). Utilizing eqns (12a–c) one gets

$$\psi_2 = \frac{1}{\sqrt{2}}\left[p_X + \frac{1}{2}(H_1 - H_2 + H_3 - H_4)\right], \tag{26b}$$

$$\psi_3 = \frac{1}{\sqrt{2}}\left[p_Y + \frac{1}{2}(H_1 - H_2 - H_3 + H_4)\right], \tag{26c}$$

$$\psi_4 = \frac{1}{\sqrt{2}}\left[p_Z + \frac{1}{2}(H_1 + H_2 - H_3 - H_4)\right]. \tag{26d}$$

Hence, the hybrid AOs completely disappeared. They are replaced by the conventional $s$, $p_X$, $p_Y$ and $p_Z$ free-atom AOs. The set of formulas (26) is a source of a widespread misconception that hybrids do not "exist." In fact, it shows only that $s$ and $p$ orbitals are a more sensible choice for the MO scheme in the highly symmetric $T_d$ system. The hybrid basis set also yields MOs of $A_1$ and $T_2$ symmetries, but the corresponding formulas (25) are more complicated. The opposite case is found in distorted tetrahedra occurring in highly strained systems. Let us consider a prototype of the angularly strained molecule cyclopropane. Two hybridization schemes were put forward to describe the strained three-membered ring. They are depicted in Fig. 7. The Coulson–Moffitt bent-bond model describes the cyclopropyl ring by hybrids which are somewhat accommodated to the small internuclear angle of 60°. Their interorbital C—C—C angle is therefore smaller than 109.5°, but of course larger than 90°, as required by eqn (22), thus forming bent bonds (BB). The Walsh model describes bond bending by tangential $p_t$ orbitals.

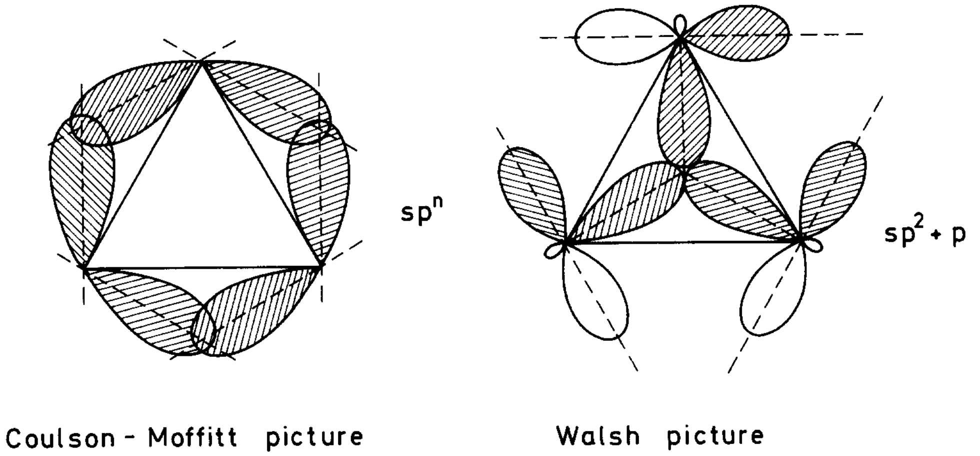

Fig. 7. Coulson–Moffitt and Walsh models for the cyclopropyl ring.

Each carbon donates in addition one $sp^2$ hybrid directed to the center of the ring. This model is widely applied in interpreting PES ionization potentials in strained cyclic and polycyclic compounds involving three-membered rings. The reader probably shares the writer's uneasy feeling caused by the unfavourable overlapping of $p_t$ orbitals, which is always a warning for a danger. It should be strongly emphasized that free-atom AOs, Coulson–Moffitt and Walsh basis sets are completely equivalent if the calculations are carried out far enough, because they are interrelated by orthogonal transformations. This, however, is not the issue. The question we would like to answer is which of the three basis sets leads most directly to the satisfactory result, or in other words, which starting point is the best in the sense of the Occam's razor principle. Heilbronner *et al.*[107] have conclusively shown by using a simple Hückel-type approach that the bent bond (BB) model yields in cyclopropane the final result in a smooth way. The final step of taking into account the configuration interaction (CI) could be safely skipped. On the contrary, the Walsh (W) basis set is considerably less convenient and only the explicit CI treatment gives acceptable results. A somewhat more complex situation appears in bicyclo(1.1.0)butane, which we shall consider now because it is a nice example of the use of symmetry arguments in discussing the electronic structure of molecules. The Walsh scheme representing the generalization of the cyclopropyl case (Fig. 8) is not compatible with the geometric structure of the molecule[108]. A refined W model consisting of the *sp* hybrids on the bridgehead carbons accompanied by a pair of $p_r$ radial and $p_t$ tangential AOs on each center is more appropriate and it will be utilized in what follows. The terminal carbon atoms are described by the $sp^2 + p_t$ basis as in cyclopropane (Fig. 8). The best BB model of bicy-

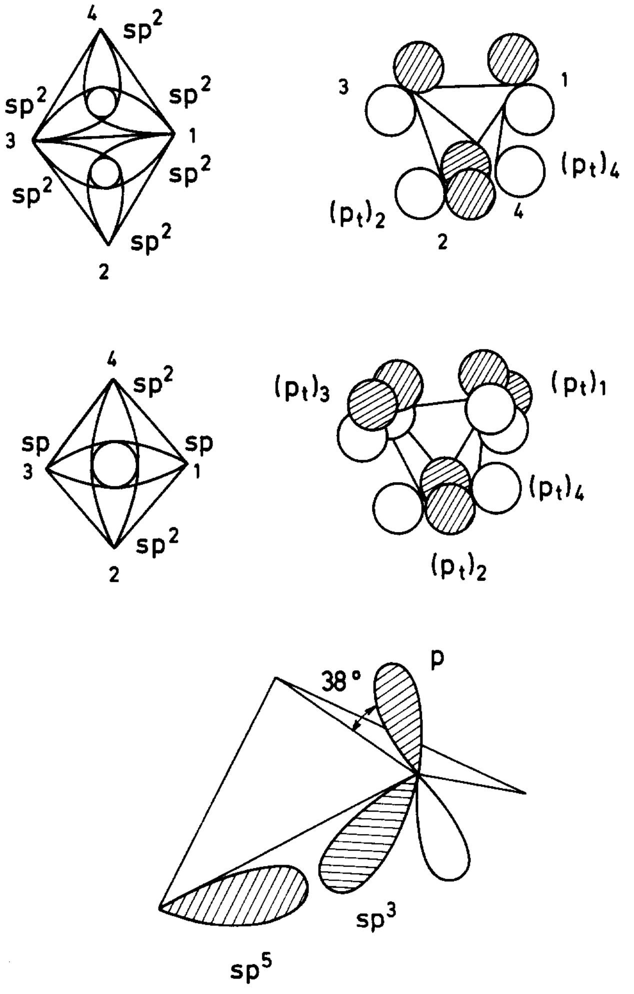

Fig. 8. Walsh and bent-bond models for the bicyclo(1.1.0)butane skeleton.

clo(1.1.0)butane is that emerging from the *ab initio* calculations of Newton and Schulman[109]. The weak central bond is described by $p$ orbitals inclined by 38° to the internuclear line, while the perimetric C—C bonds are formed by the $sp^3$–$sp^5$ hybrids (Fig. 8). We shall try to describe the carbon skeleton by the semilocalized molecular orbitals (SLMO) belonging to irreducible representation of the $C_{2v}$ point-symmetry group† by using BB and W basis sets. In order to make a fair comparison between these two basis sets, we shall slightly adjust the W model and use the $sp^{0.5}$ hybrid at the bridgeheads. Then the adopted BB model and W basis correspond to identical hybridization states[108]. For example, the bridge bond is given by the same $p$ orbital inclined by 38°, etc. The SLMOs are readily obtained by inspection of the table of characters for the $C_{2v}$ group[62]. The orbital composition of SLMOs is schematically displayed in Fig. 9. Several comments are in place here. The energy scale is not the same for the BB- and W-SLMO levels. It can be easily shown that $1'a_1$, $1a_2$ and $2'a_1$ levels of $A$ symmetry are equal for both models because the corresponding SLMO functions are identical. The $1'a_1$ and $2'a_1$ wavefunctions are of the $A_1$ symmetry and can mix together. Their + and − combinations yield the most stable and the highest occupied MO (HOMO) orbitals, respectively. It is obvious by using a simple overlapping argument that the $1'a_1$ and $2'a_1$ orbital schemes depicted in Fig. 9 give the dominant contribution to the corresponding correct SLMO. The former are given for

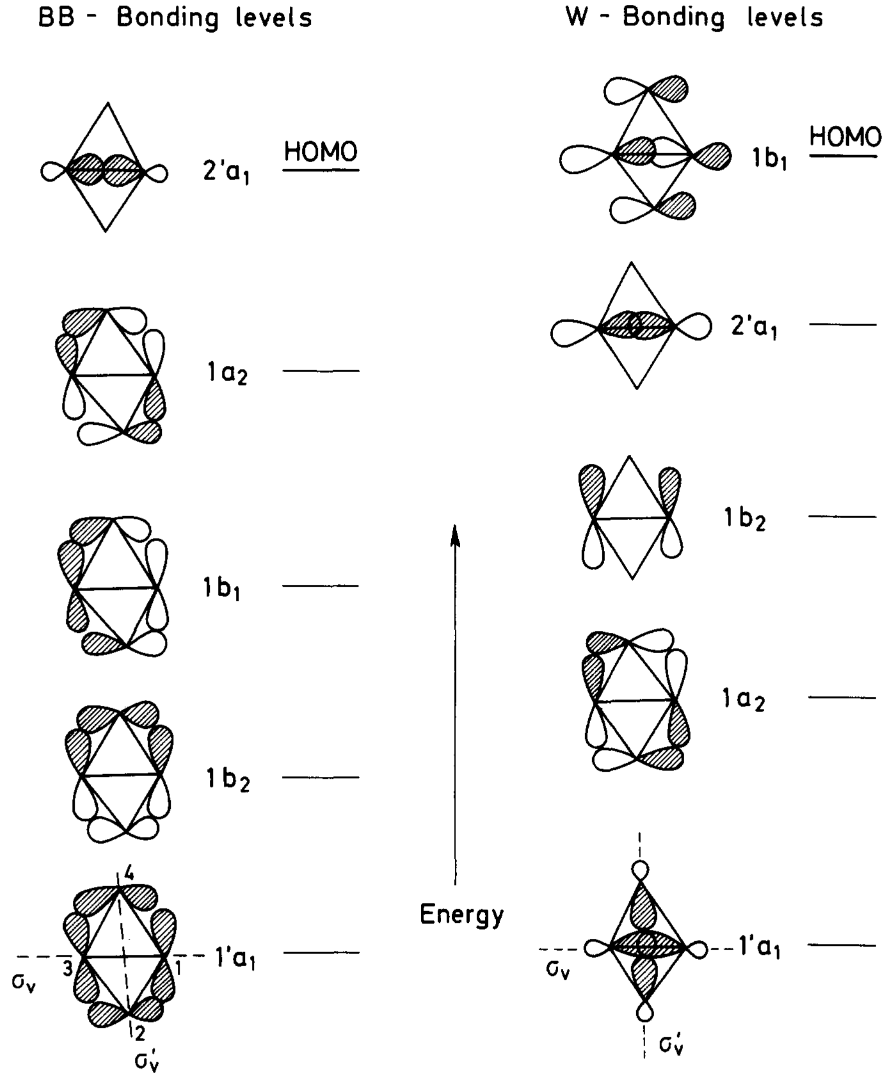

Fig. 9. Semilocalized molecular orbitals of the bicyclo(1.1.0)butane skeleton obtained by using BB and W models.

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†These are symmetry-adapted linear combination of basis set functions, or SALCs in Cotton's terminology[60].

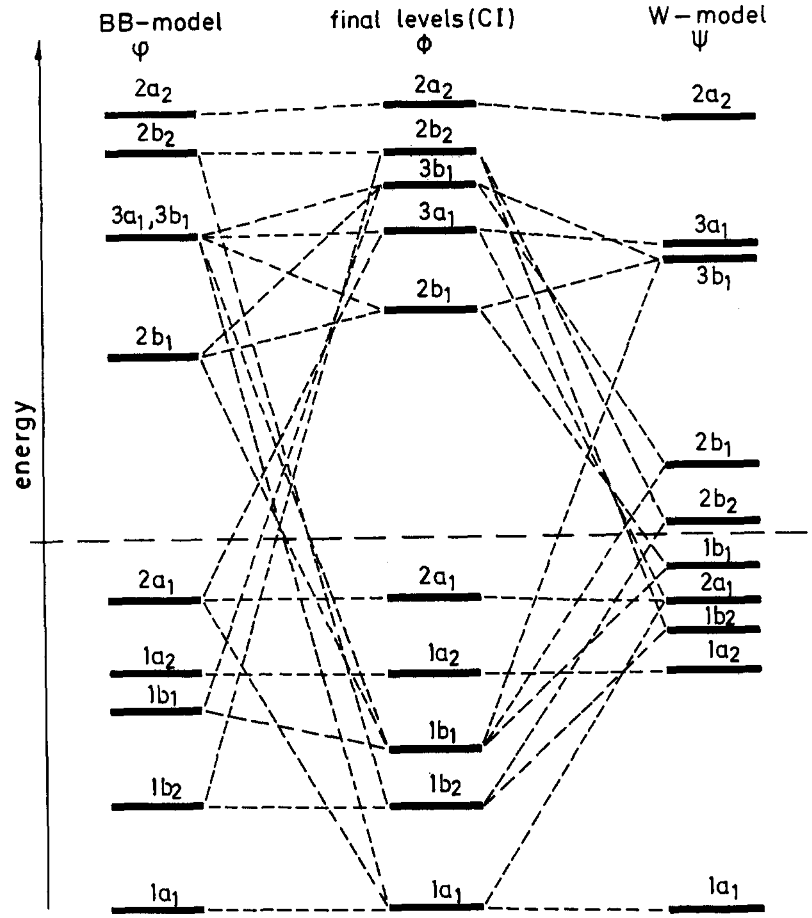

Fig. 10. One-electron CC levels in bicyclo(1.1.0)butane.

better inspection. The ordering of the SLMOs is easily obtained by assuming that intraring overlap is more important than the transannular overlapping. One observes that the BB and W schemes predict different symmetries for HOMOs. It will appear in a later stage that the BB-SLMO ordering is correct. A simple and plausible parametrization within the framework of the model Hamiltonian of the Hückel-type provides quantitative estimates of the SLMO levels[108]. Furthermore, CI with virtual levels yields the final one-electron eigenvalues and eigenvectors. They are the same (Fig. 10) for both BB and W models, as expected since the corresponding basis sets are related by a simple orthogonal transformation. However, the ordering of the BB-SLMOs is preserved by the CI, while considerable reordering of the W-SLMOs is necessary to obtain the final result. The W-SLMOs of the $b_1$ and $b_2$ symmetries are by far too unstable. This is a consequence of the shift of $s$ character to the virtual (unoccupied) levels of the same symmetries, which in turn are too low. A serious difficulty faced by the application of the W basis is caused by the symmetry characteristics of the $p_t$ orbitals. They are antisymmetric relative to the symmetry plane passing through the terminal carbon atoms. Hence they have to disappear in the $1b_2$ W-SLMO wavefunction. The hybrid AOs in the BB model are much more flexible. A pair of hybrids emanating from the same carbon can either assume the same sign or adopt the opposite signs. Concomitantly, apart from the HOMO, B-SLMOs have four nice intrabond overlaps, and are thus more physically acceptable and aesthetically pleasing. Since the BB scheme is a better and more realistic starting point, the final CI may be omitted for qualitative purposes. Importance of this finding lies in the fact that hybrid AOs are highly transferable between the similar moieties, and the symmetry reasoning displayed above can give enlightening insight into the ordering of the one-electron levels. The moral of the story is that a shrewd choice of the basis set accompanied by symmetry arguments can save a lot of computational efforts.

### *Miscellaneous molecular properties and hybridization*

Compton profiles depend on the momentum distribution in a molecule[110]. The latter exhibits additivity in well-localized systems, which can be interpreted in terms of LMOs and in *ultima linea* by hybridization[111–113]. It appears that the average momentum of, for example, the C—H bond increases with the $p$-orbital population in a hybrid[110,111].

Bond stretching frequencies and force constants show hybridization dependence[47,79,104,105]. Hybrid orbitals seem to be a natural choice for a basis set in force-field methods, but some care has to be exercised due to the incomplete orbital following of the nuclear motions[114]. Molecular total (and bond) dipole moments depend dramatically on hybridization[79,115], but the charge migration contribution is also very important. The same conjecture is valid for electric field gradients and the corresponding asymmetry parameters[116,117]. Magnetic properties like diamagnetic shielding ($\sigma^d$) of the nuclei and diamagnetic susceptibility of molecules ($\chi^d$) are indirectly dependent on hybridization via molecular geometry. Simple approximate formulas involving only interatomic distances were suggested for the calculation of these entities. The results of the IMO method based on local hybrid orbitals for $\sigma^d$ and $\chi^d$ in hydrocarbons are in good accordance with observed values and/or *ab initio* data[51].

## SYMMETRY, HYBRID ORBITALS AND MORE INVOLVED MOLECULAR WAVEFUNCTIONS

The exploitation of symmetry in complex quantum-chemical calculations of molecular wavefunctions is of utmost importance. The reader is referred to the illuminating discussion of the factorization of secular equations by Byers Brown[118], and a review article on symmetry adaptation and applications of Wigner–Racah algebras in quantum chemistry by Kibler[119]. We shall confine our discussion here to the choice of the symmetry-adapted functions at the atomic level. It is intuitively clear that the use of the chemically adjusted hybrid AOs must be advantageous in incomplete (simple) VB and MO calculations. The preceding discussion of the BB basis in describing carbon skeletons in cyclopropane and bicyclo(1.1.0)butane was very illustrative in this respect. Indeed, if we employ incomplete sets and the interactions are treated only to a certain degree of accuracy, then the starting point becomes extremely important. The atomic basis set should in this case reflect the salient features of the molecular environment, the local symmetry being the most important one. The first use of the polarized (i.e. hybrid) AOs can be traced to the 1930s. Dickinson[120] and Rosen[121] employed the ($1s_H$ + $2p_H$) basis for the calculation of ground states of $H_2^+$ and $H_2$ systems, respectively. The *ab initio* MO studies based on the hybrid AO sets are rather sparse. The early work of Hoyland[122] on hydrocarbons and of Petke and Whitten[123] on small heteroatomic molecules should be mentioned. The simulated *ab initio* scheme[124] relies on the transferability of the matrix elements from smaller fragment molecules to larger systems. It is much easier to keep track of transferable matrix elements in hybrid basis sets, because they are independent of the choice of the coordinate systems. The role of hybrid AOs in VB and GVB[32,38,42] methods was already mentioned. It should be pointed out, however, that the use of hybrid orbitals within the VB function gives a fair approximation to the linear combination of several VB configurations[125]. The group function method of McWeeny and Klessinger[126] involves full CI within the limited basis of two local hybrid AOs belonging to a given bond geminal. The total electronic wavefunction is written then as an antisymmetrized product of pair functions describing inner core, bond and lone pairs of electrons[126,127]. It is a pity that this approach did not enjoy more applications.

Properly adjusted hybrid orbitals are local wavefunctions of the zeroth order. Notwithstanding their remarkable properties, hybrid basis sets did not find widespread use in semiempirical theories of chemical bonding. They are, however, pivotal in the simple maximum overlap[128,129] or iterative maximum overlap[46,51,71,73,75,81,83,84] procedures. The former can be employed only if the geometry of molecules is known, which is a serious drawback. The hybrid-based MO schemes were used by Fukui and coworkers[130] in discussing molecular properties and reactivity. A conceptually important semiempirical method was devised by French researchers[131,132]. It is called PCILO because the localized MOs formed by hybrid orbitals undergo a perturbational procedure in order to take into account configuration interaction.

Unfortunately, the integral approximation scheme is borrowed from the CNDO method, which should be considered as a "*Schönheits Fehler*." The structure of the method indicates that PCILO will be effective in well-localized systems, and not unexpectedly in this type of compounds it gives useful results. Current semiempirical MO approaches disregard the local symmetry-adapted basis sets, which seems to be a source of considerable difficulties. There are arguments which indicate that various zero-differential overlap (ZDO) approximation schemes can be justified, at least to a large extent, if a basis set of uniformly (or Löwdin) orthogonalized hybrid AOs is utilized[133,134]. Finally, it should be mentioned that hybrid basis sets proved very useful in approximate calculations of the electronic structure and properties of covalent solids[135,136].

We shall note in passing that hybridization is an important concept in interpreting intricate molecular wavefunctions. The hybridization indices can be extracted from the first-order density matrix elements[44,68,137–139], and compared with results obtained by more elementary procedures involving hybrid orbitals which are built in the model. This is a remarkable result because the one-determinantal wavefunction (2) is invariant to all orthogonal transformations of the basis set and yet the directional properties of bonds are stored in its density matrix. It is a rather fortunate feature, too, because otherwise the single determinants would not be acceptable wavefunctions for a description of chemical bonding.

## FINAL REMARKS AND CONCLUSIONS

Hybridization is a very old concept created by men to describe a new property by using the well-known entities. In ancient Greece, a Centaur (Fig. 11)[140] was coined using an unmutilated human torso and the body of a horse, in an artistic attempt to represent a hillbilly. Even older examples of nowadays unusual hybrid creatures can be found in Egyptian mythology. It is likely that the idea of hybridization emerged by observing hybrid animals and plants in nature. It is also not surprising that the hybridization is used today in the biosciences; among these we mention only hybridoma cells obtained by a fusion of lymphocytes with plasma-cytoma cells[141,142]. The former produce a specific antibody, while the latter are immortal. Their hybrids are capable of producing monoclonal antibodies *ad infinitum*. This discovery was awarded a Nobel Prize for Medicine in 1984.

Hybridization in chemistry is an intellectual model designed to describe directional features of chemical bonds. A hybrid orbital formed by $s$, $p$, . . . AOs has certain characteristics of

Fig. 11. Centaur in fight.

each component and yet exhibits remarkable new properties which are not inherent to pure AOs. Hybrids not only rationalize a large part of stereochemistry, but provide simple explanations for a number of otherwise unrelated observables, thus suggesting some underlying authenticity of the model. This "grain of truth" is to be ascribed, at least partly, to the symmetry content of hybrids. They are adapted to conform with the local symmetry of an atom in a molecular environment. The bonding power of the hybrids is increased by the use of additional criteria like maximum bond strength or overlapping. These simple criteria and slight empirical adjustments significantly augment the performance of the model. One can find full analogy with the crystal field theory, where the symmetry represents a backbone of the approach and the semiquantitative agreement with experiment is achieved after some parametrization. Hybridization and localized molecular orbitals have considerable epistemological importance because they provide one of the cornerstones of the quantum theory of chemical bonding and valence. They describe and explain the most important axiom of the experimental chemistry—the chemical bond, which is a firm and well-established empirical concept. It is impossible to derive the concept of a chemical bond from the first principles. Hence, the hybridization is an important link between the rigorous quantum theory of molecules and phenomenology. It is difficult to find a simpler concept which is so rich in chemical information and has at the same time such a pervasive interpretative power. In my opinion, there are still nuggets waiting to be picked up in a gold field called hybridization, particularly within the framework of the semi-empirical theories of molecules and crystals.

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