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On the Complex Hybridization of Orbitals of *s* and *p* Type

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The direction of valence is defined as the direction from the atomic nucleus to the center of gravity of the hybrid density. Complex mixing coefficients of the orbitals of pure angular momentum are introduced in the hybrid. This allows a considerable extension of the hybridization concept with regard to valence angles and equivalence restrictions. General expressions for the direction consines of valence and for bond angles are given, and applications are made to several molecules with bond angles of 90 degrees or less.

Die Valenzrichtung eines Hybrids wird als die Richtung vom Atomkern zum Schwerpunkt der Elektronendichte difiniert. Dabei werden auch komplexe Koeffizienten für die atomaren Zustandsfunktionen zugelassen, wodurch eine erhebliche Erweiterung des Hybridisierungskonzeptes im Hinblick auf Valenzwinkel und Nebenbedingungen infolge von Äquivalenz möglich ist. Allgemeine Ausdrücke für die Richtungskosinus und Bindungswinkel werden angegeben, ebenso einige Beispiele für Moleküle mit Winkeln unter 90°.

La direction de valence est définie comme la direction joignant le noyau atomique au centre de gravité de la densité de l'hybride. Des coefficients de mélange complexes sont introduits dans l'hybride pour les orbitales de moment angulaire pur. Ceci permet une extension considérable du concept d'hybridation en ce qui concerne les angles de valence et les restrictions d'équivalence. Des expressions générales pour les cosinus directeurs des directions de valence et pour les angles de liaison sont obtenues et appliquées à plusieurs molécules dont les angles de liaison sont au plus de 90°.

Introduction

Concepts such as directed valence and valence angle are extremely important and real entities to the chemist and it has been and still is an important task for the quantum chemist to furnish theoretical models from which such properties can be calculated or qualitatively understood.

Quantum mechanical applications to problems of molecular structure generally employs states of the total system constructed from one-electron states of the participating atoms. This holds for the molecular orbital as well as the valence bond approach and their simplest extensions. Atomic orbitals can be formed in a variety of ways. The simple idea of mixing atomic functions of different symmetries to form so called hybrids [1, 2, 3] has been found to be very useful for describing symmetries in molecular binding. The hybridization procedure has been extremely valuable in giving a simple explanation of the valence concept and a first crude description of the geometry of inorganic as well as organic compounds. Even if the hybrids are not essential or even necessary for a molecular orbital calculation yielding bond distances and bond angles, they still are so useful for the chemist in getting a rough idea of the electronic structure of the bonding situation that the hybridization idea warrants further studies.

Preliminaries

Starting with a set of atomic orbitals being eigenfunctions of angular momentum, proper linear combinations can be formed. These constitute the hybrid orbitals (hybrids), each with a largest extension in a specified direction. From one s and three p orbitals (p_x; p_y; p_z) four linearly independent hybrids, h_1, h_2, h_3 and h_4, can be formed.

$$h_k = \sum_{i=l}^{4} a_{ki} \Phi_i \, . \tag{1}$$

In the coefficient matrix

$$\boldsymbol{a} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix} \tag{2}$$

each row corresponds to a hybrid. The set of atomic orbitals we start from are orthonormal, and we can retain this property for the hybrids if $\boldsymbol{a}$ is chosen to be a unitary matrix, i.e.

$$\boldsymbol{a}^{\dagger} \boldsymbol{a} = \boldsymbol{a} \boldsymbol{a}^{\dagger} = 1$$

or

$$\sum_{i=l}^{4} a_{ik} \, a_{il}^{*} = \sum_{i=l}^{4} a_{ki} \, a_{li}^{*} = \delta_{kl} \, . \tag{3}$$

It is easily shown that for a real matrix $\boldsymbol{a}$ (orthogonal) the angle θ_{kl} between the directions of the hybrids h_k and h_l fulfils the relation

$$\gamma_{kl} = \cos \theta_{kl} = - \frac{a_{k1} \, a_{l1}}{[(1 - a_{k1}^2)(1 - a_{l1}^2)]^{1/2}} \, . \tag{4}$$

In applications, a_{ki} have been restricted to real values and the phase of h_k fixed so that $a_{k1} \geq 0$. From Eq. (4) follows then that $\gamma_{kl} \leqq 0$ which shows that in this way valence angles less than 90 degrees can not be described. This means that molecules like cyclopropane and its hetero-analogues, tricyclobutane derivatives, and phosphorus as P_4 can not be given a satisfactory description in terms of hybrids. Other limitations are that *equivalency* is restricted to the case when all a_{k1} are equal to $\frac{1}{2}$ which indicates that four equivalent hybrids can be constructed only for the case of tetrahedral valence angles. (For planar systems when one π-orbital is separated we have three equivalent hybrids only for the pure trigonal case.) Moreover, when three hybrids are determined as to their directions, the direction of the fourth hybrid follows from the orthogonality (unitarity) conditions.

Serious attempts have been made to override the shortcomings connected with the angular conditions expressed in Eq. (4). Strongly related to this are the ideas about bent bonds discussed by several authors [2, 4]*. The very natural generali-

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* It has been pointed out by W. WELTNER, JR.: J. Amer. chem. Soc. **75**, 4224 (1953) (Footnote 38) that the original calculations by C. A. COULSON, and W. E. MOFFIT: Phil. Mag. **40**, 1 (1949), on Cyclopropane where they found it necessary to invoke bent bonds, were incorrect.

zation of allowing for complex matrix elements a_{ik} has been suggested by LÖWDIN [5] but no analysis has been made of the possibilities of such a generalization.

In the next section we introduce a general unitary transformation matrix and a new definition of valence direction, which will prove to be identical with the already accepted definition for the case of *real hybrids*. Applications are made to tricyclobutane, cyclopropane and tricyclooctane (cubane).

Derivation of Basic Formulae

For *real* hybridization matrix (all a_{ki} real) the hybrids have the characteristics of vectors in three dimensional Euclidean space. This means that the function space and the space of molecular geometry in a certain sense are identical. For complex functions this is not so and we have to redefine what we mean with an angle between hybrids.

Since geometry of molecules are based on real quantities we study the hybrid densities $|\, h \,|^2$ rather than the hybrids themselves. To each hybrid we associate a direction defined by the vector from the origin (the atomic nucleus) through the center of gravity of the density.

Our basis functions are of s and p type and can be written as:

$$\Phi_1 = s = s(r)\,, \qquad \begin{aligned} \Phi_2 &= p_x = f(r)\,\frac{x}{r}\,,\\ \Phi_3 &= p_y = f(r)\,\frac{y}{r}\,,\\ \Phi_4 &= p_z = f(r)\,\frac{z}{r}\,. \end{aligned} \tag{5}$$

The hybrids are expressed as:

$$h_k = a_{k1}\,s + f(r)\left[a_{k2}\,\frac{x}{r} + a_{k3}\,\frac{y}{r} + a_{k4}\,\frac{z}{r}\right]$$

in which the a_{ki}'s are complex numbers.

The direction cosines of h_k are then defined to be

$$\gamma_{k\mu} = \frac{\langle h_k \mid \mu \mid h_k\rangle}{\bigl[\sum\limits_{\nu=x,\,y,\,z} \langle h_k \mid \nu \mid h_k\rangle^2\bigr]^{1/2}}\,, \qquad \mu = x, y, z\,. \tag{6}$$

In the evaluation of the integrals in expression (6) we observe that only mixed terms of sp^* type give nonvanishing contributions and that furthermore the directions cosines $\gamma_{k\mu}$ are independent of the radial integrals $\int\limits_0^\infty s(r) f^*(r) r^3 dr$.

Expressed in the coefficients a_{ki}, Eq. (6) will read

$$\gamma_{k\mu} = \frac{\mathrm{Re}\{a_{k1} a^*_{k\mu}\}}{\left[\sum\limits_{\nu=2}^{4} (\mathrm{Re}\; a_{k1}\, a^*_{k\nu})^2\right]^{1/2}} \qquad \mu = x, y, z\,.^{\star} \tag{7}$$

The cosine for the valence angle θ_{kl} defined by the hybrids h_k and h_l is

$$\gamma_{kl} = \cos\,\theta_{kl} = \sum_\mu \gamma_{k\mu}\,\gamma_{l\mu} =$$

$$= \frac{\sum\limits_\mu \mathrm{Re}\{a_{k1} a^*_{k\mu}\}\mathrm{Re}\{a_{l1}\, a^*_{l\mu}\}}{\bigl[\sum\limits_\nu (\mathrm{Re}\{a_{k1}\, a^*_{k\nu}\})^2 \cdot \sum\limits_\mu (\mathrm{Re}\{a_{l1}\, a^*_{l\mu}\})^2\bigr]^{1/2}} \tag{8}$$

[⋆] We are using Greek indices to run interchangably over 2, 3, 4 or x, y, z respectively.

If the a_{ki}'s are real, applications of the proper orthogonality relations (3) will reduce expression (8) to the simple form given in Eq. (4). This shows that the treatment given here encompasses the conventional hybridization ideas.

We can prove that all four valences cannot occur in the same half space. If, for instance, all the hybrids were pointing into the half space defined by all points having positive x-coordinates ($x > 0$), then all direction cosines γ_{kx} would be positive. However, from Eq. (7) we find

$$\gamma_{kx}\,\alpha_k = \operatorname{Re}\{a_{k1}\,a_{k2}^*\}$$

where

$$\alpha_k = [\sum_{\nu=2}^{4} (\operatorname{Re}\{a_{k1}\,a_{k\nu}^*\})^2]^{1/2} \geq 0$$

and when we sum over k we obtain

$$\sum_{k=1}^{4} \gamma_{kx}\,\alpha_k = \operatorname{Re}\,(\sum_{k=1}^{4} a_{k1}\,a_{k2}^*) = 0\,.$$

The right hand member vanishes since it just is the real part of one of the orthogonality relations (3). This must then lead to the conclusion that all the γ_{kx} can not have the same sign i.e. all four valencies can not occur in the same half space defined by the coordinate axis.

If we were given the expansion coefficients a_{ik} we could calculate the corresponding valence angles. Another question is how the complex matrix elements can be inferred from known molecular geometry.

A general unitary matrix of order 4 by 4 can be expressed by 16 real parameters. If we write the matrix elements as $a_{jk} = r_{jk} \exp(i\varphi_{jk})$ we could in particular pick as independent quantities 6 absolute values, r, and 10 arguments, φ.

If we return to the Euclidian space in which the four valences are located, we find that their directions are completely determined by 8 direction cosines, two for each of the four directions. This can also be expressed so that 5 valence angles give the mutual positions of the four valence directions in space and this system is fixed in space by giving three additional angles, e.g. two of which determine the direction of one of the valences and the third the rotation about this axis.

Superficially we then have at our disposal twice as many variables as we can specify from a given geometry. However, we can always multiply each hybrid orbital by an arbitrary phase factor without changing the hybrid density or anything else of physical significance nor will this effect the unitarity of the transformation matrix. This means that we can always choose the first column of $\boldsymbol{a}$ real and positive.

For the direction cosine of valence k with axis μ we obtain

$$\gamma_{k\mu} = \frac{r_{k\mu} \cos \varphi_{k\mu}}{[\sum_{\nu=2}^{4} (r_{k\nu} \cos \varphi_{k\nu})^2]^{1/2}}$$

which is independent of r_{k1}. For γ_{kl}, the cosine of the angle between valences k and l we then have

$$\gamma_{kl} = \sum_{\mu=x,y,z} \gamma_{k\mu}\,\gamma_{l\mu}\,.$$

These basic equations are used in the next section to derive the hybridization matrix $\boldsymbol{a}$ for some typical cases which could not be properly described by the conventional real hybrids.

Examples: If we restrict the treatment to the case of four equivalent hybrids we can choose all $r_{k1} = \frac{1}{2}$. The remaining independent matrix elements are then possible to determine from the unitarity conditions and the valence angles or rather the direction cosines, once a coordinate system is chosen.

For valence angles greater than 90 degrees it is always possible to have real mixing coefficients but for non-equivalent hybrids the present idea may also in this case lead to useful generalizations.

1. Cyclopropane $(\underline{\mathrm{CH_2CH_2CH_2}})$. If the bonds from each carbon atom to the hydrogen atoms are placed in the xy plane symmetrically about the x axis with a valence angle of 120 degrees, and the bonds to the other two carbon atoms in the ring are in the xz plane, forming a valence angle of 60 degrees, (Fig. 1), the hybrids are given by the following matrix:

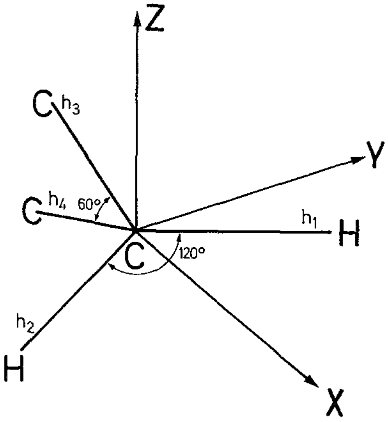

Fig. 1

$$\begin{bmatrix} \frac{1}{2}, & \frac{1}{2}\cdot\left(\sqrt{\frac{2}{3}} + i\sqrt{\frac{1}{3}}\right), & \sqrt{\frac{1}{2}}, & 0 \\ \frac{1}{2}, & \frac{1}{2}\cdot\left(\sqrt{\frac{2}{3}} + i\sqrt{\frac{1}{3}}\right), & -\sqrt{\frac{1}{2}}, & 0 \\ \frac{1}{2}, & -\frac{1}{2}\cdot\left(\sqrt{\frac{2}{3}} + i\sqrt{\frac{1}{3}}\right), & 0, & \sqrt{\frac{1}{2}}\cdot\left(\frac{1}{3} + i\frac{2\sqrt{2}}{3}\right) \\ \frac{1}{2}, & -\frac{1}{2}\cdot\left(\sqrt{\frac{2}{3}} + i\sqrt{\frac{1}{3}}\right), & 0, & \sqrt{\frac{1}{2}}\cdot\left(\frac{1}{3} + i\frac{2\sqrt{2}}{3}\right) \end{bmatrix}$$

2. Tricyclooctane (cubane)$\cdot(\mathrm{C_8H_8})$. The valences of carbon in this molecule are described by the matrix:

$$\begin{bmatrix} \frac{1}{2}, & \frac{\sqrt{3}}{2}, & 0, & 0 \\ \frac{1}{2}, & -\frac{2}{2\sqrt{3}}, & 0, & \sqrt{\frac{2}{3}}\cdot\left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) \\ \frac{1}{2}, & -\frac{1}{2\sqrt{3}}, & \frac{1}{\sqrt{2}}\cdot\left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right), & -\frac{1}{\sqrt{6}}\cdot\left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) \\ \frac{1}{2}, & -\frac{1}{2\sqrt{3}}, & -\frac{1}{\sqrt{2}}\cdot\left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right), & -\frac{1}{\sqrt{6}}\cdot\left(\frac{1}{2} + i\frac{\sqrt{3}}{2}\right) \end{bmatrix}$$

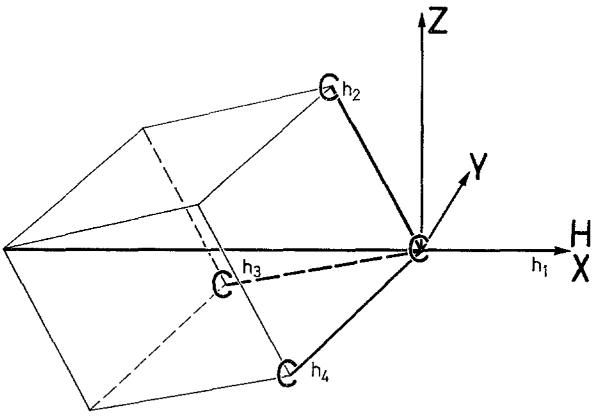

Fig. 2

Applying the formulae for the direction cosines it is easily checked that the bond to the hydrogen atom is directed along the x axis, which is opposite to the direction of the diagonal of the cube, the edges of which are formed by the three remaining valences. The direction of the second hybrid, h_2, lies in the xz plane (see Fig. 2).

3. Tricyclobutane (C_4H_4) *and Phosphorus* (P_4). In these molecules the carbon and phosphorus atoms respectively form a regular tetrahedron, the difference being that in P_4 the hybrid h_1 is occupied by a lone pair and does not take part in bond formation. The first hybrid is directed along the x axis and the rest form a corner in the tetrahedron with h_2 in the xz plane (Fig. 3).

$$\begin{bmatrix} \frac{1}{2}, & \frac{\sqrt{3}}{2}, & 0\,, & & 0 \\ \frac{1}{2}, & -\frac{1}{2\sqrt{3}}, & 0\,, & & \sqrt{\frac{2}{3}}\cdot\left(\frac{1}{4}+i\frac{\sqrt{15}}{4}\right) \\ \frac{1}{2}, & -\frac{1}{2\sqrt{3}}, & \frac{1}{\sqrt{2}}\cdot\left(\frac{1}{4}+i\frac{\sqrt{15}}{4}\right), & & -\frac{1}{\sqrt{6}}\cdot\left(\frac{1}{4}+i\frac{\sqrt{15}}{4}\right) \\ \frac{1}{2}, & -\frac{1}{\sqrt{23}}, & -\frac{1}{\sqrt{2}}\cdot\left(\frac{1}{4}+i\frac{\sqrt{15}}{4}\right), & & -\frac{1}{\sqrt{6}}\cdot\left(\frac{1}{4}+i\frac{\sqrt{15}}{4}\right) \end{bmatrix}$$

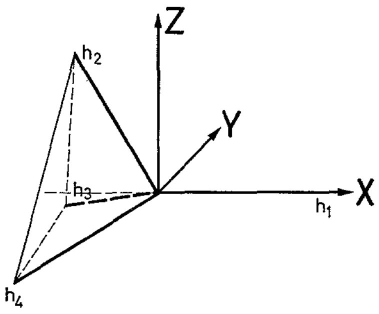

Fig. 3

4. Xenon Tetrafluoride XeF_4. The unitary complex matrix

$$\begin{bmatrix} \frac{1}{2}, & \frac{1}{2}i, & \frac{1}{\sqrt{2}}, & 0 \\ \frac{1}{2}, & \frac{1}{2}i, & -\frac{1}{\sqrt{2}}, & 0 \\ \frac{1}{2}, & -\frac{1}{2}i, & 0, & \frac{1}{\sqrt{2}} \\ \frac{1}{2}, & -\frac{1}{2}i, & 0, & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

expresses four valences with valence angles of 90 degrees, all in the yz plane. This could be used for a molecule like XeF_4, which is square and planar with the xenon atom in the center.

Comment

Many interesting problems arise in connection with the generalizations of the hybridization concepts suggested here, particularly the problem of equivalency where we think that further generalizations can be made. We hope to report on these results in a forthcoming paper.

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