Hybrid Bond Orbitals and Bond Strengths for Pentacovalent Bonding

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A brief history of the theory of hybrid bond orbitals is presented. Bond strengths and hybrid bond orbitals are derived for pentacovalent systems having five bond directions which are related by five-, four-, or threefold axes of symmetry. In none of these cases does the maximum value of the bond strength occur for the geometry in which the central atom is coplanar with the non-axial bonds. For the system with a threefold axis of symmetry, the curve of bond strength *versus* bond angle is sufficiently flat over a large range of angles that the non-axial bonds are amenable to bending. Finally, the experimental implication of these results is discussed.

I. INTRODUCTION

Relatively little experimental information about pentacovalent bonding appears in the literature, this being especially so for pentacovalent bonding involving the transition elements. Owing to this paucity of experimental data, not much application of the conventional computational techniques based on molecular-orbital theory has been made to explain or predict the bonding characteristic of pentacovalency. Nevertheless, simple valence-bond theory can be applied to delineate the three types of coordination geometries with axial symmetry. These are: (1) five single bonds with a 5-fold axis of symmetry (pentagonal pyramidal structure, point group C_{5v}); (2) five bonds with a 4-fold axis of symmetry (tetragonal pyramidal structure, point group C_{4v}); and (3) five bonds with a 3-fold axis of symmetry (point group C_{3v}). Five bonds equivalent by geometrical symmetry operations occur for the 5-fold axis, four equivalent bonds and one non-equivalent bond for the 4-fold axis, and three equivalent bonds and two non-equivalent or equivalent bonds for the threefold axis. In this paper simple valence-bond theory is employed to investigate the relative bonding efficacy for each of these structures.

The theory of hybrid bond orbitals was formulated in 1931 by one of us and reported in the paper *The Nature of the Chemical Bond. Application of Results Obtained from the Quantum Mechanics and from a Theory of Paramagnetic Susceptibility to the Structure of Molecules*[1]. This paper established the framework for understanding the electronic and geometric structure of molecules and ions in terms of hybrid bond orbitals. By employing the Lagrange method of undertermined multipliers, hybrid bond orbitals were derived for

particular molecular systems through the maximization of the appropriate linear combination of atomic eigenfunctions in the bond directions subject to the restriction of orthonormality and the assumption that the linear combination is independent of the difference in radial dependence displayed by atomic eigenfunctions having different values of the angular momentum quantum number. The strength, S, of a hybrid bond orbital was defined as the value in the bond direction of the angular part of the bond orbital, normalized to 4π over the surface of a sphere. The bond strength is a measure of the energy gained through bond formation; the greater the value of S, the more energetically favorable is the bond. This treatment led to an understanding of the structure and properties of molecules formed by the first-row elements, with emphasis on the tetrahedral angle, which is of fundamental importance in the bonding displayed by these elements. This paper also treated certain special cases involving spd hybrid bond orbitals.

In 1932 Hultgren[2] studied the problem of the best possible sets of sp^3d^5 orbitals having a cylindrical axis of symmetry, and in 1940 Kimball[3] showed how spd hybrid bond orbitals possessing the symmetry of the common point groups could be derived in terms of group theory. Shirmazan and Dyatkina[4] and Eisenstein[5] later extended this group-theoretical approach to $spdf$ hybrid bond orbitals. The theory of hybrid bond orbitals was applied to elucidate the structure of $Mo(CN)_8^{4-}$ by Racah[6] in 1943, to quadricovalent complexes of certain transition metal ions by Kuhn[7] in 1948, and to hexacovalent bonding[8], tetragonal antiprismatic bonding[9], bipyramidal heptacovalent complexes such as IF_7 [10], dodecahedral octacovalent complexes[11], and tripyramidal complexes[12] by Duffey in the years 1949—1951. Deviations from the ideal tetrahedral angle for sp hybrid bond orbitals were investigated by Torkington[13] in 1951. The theory of hybrid bond orbitals was employed to study the origin of the potential barriers to internal rotation in molecules by Pauling[14] in 1958 and to bonding in icosohedral complexes by Macek and Duffey[15] and in cuboctahedral complexes, such as UB_{12}, by Canon and Duffey[16] in 1961. An analysis of the consequences of emploing complex orbitals in the theory was presented by Mårtensson and Öhrn[17]. A thorough discussion of the applications of the theory of hybrid bond orbitals and valence-bond theory is to be found in *The Nature of the Chemical Bond*[18].

Concomitant with the intense experimental activity in recent years in the fields of synthesis and characterization of compounds of the transition metals and of the lanthanide and actinide elements, much new work has been done in the theory of hybrid bond orbitals towards developing a sound and simple theory for the structure and behavior of these compounds. In the beginning of the last decade, two papers[19,20] were published on sets of five equivalent d orbitals, and in 1970, McClure[21] found a solution to the problem of deriving the best set of nine spd hybrid bond orbitals, without any restriction on the nature of the orbitals or on their relative directions in space. McClure also showed that one could derive sets of hybrid bond orbitals without imposing the restriction of equivalent radial dependence in the atomic basis set, but at the cost of much increased mathematical insight and little extra return of chemical insight. Then in 1973, Pauling and Keaveny[22] showed that the apparent incompatibility in size of the d atomic orbitals compared to that of the s and p atomic orbitals could be resolved in terms of the expansion and contraction of the d atomic orbitals in the process of bond formation.

Beginning in the middle of the past decade, one of us wrote a series of papers[23-33] which significantly extended our understanding of the bonding displayed in compounds of the transition metals and in compounds of the lanthanide and actinide elements. The best sets of two orthonormal spd hybrid bond orbitals were derived as a function of the bond angle made between their respective directions such that the spd hybrid bond orbitals achieve the maximum possible bond strength S in the two directions of this angle[24-26]. The maximum value of S, 3, occurs at the characteristic bond angles $\alpha = 73.15°$ and $\alpha = 133.62°$ (as compared with a maximum value of $S = 2$ at the characteristic tetrahedral angle for the best two orthonormal sp hybrid bond orbitals). For the best set of two orthonormal $spdf$ hybrid bond orbitals[25] the absolute maximum in S has the value 4 and occurs at the characteristic bond angles $\alpha = 54.88°$, $100.43°$, and $145.37°$.

In order to alleviate the often complicated and laborious calculation of the exact bond strength for complex systems, an approximate method for determining the bond strength (the »pair-defect-sum approximation«) was developed[24,25]. By employing the pair-defect-sum approximation, it was discovered that there exists one additional coordination polyhedron which has very nearly the same average bond strength as that for the McClure polyhedron[24,33].

The theory of hybrid bond orbitals and simple valence-bond theory have also been applied to elucidate the bond lengths in maximum-valence transition--metal compounds[23], the metallic valences of the heavier transition elements[27], the structure of transition-metal cluster compounds[28], the bond angles in transition-metal tricarbonyl compounds[29], tetracarbonyl compounds[30], and pentacarbonyl compounds[31], covalent chemical bonding in certain minerals[32], and the nature of the bonds formed by the transition metals with hydrogen, carbon, and phosphorus[31] and in bioorganic compounds[33]. A systematic investigation of the pair-defect-sum approximation[34] and review articles[33,35,36] concerning recent developments in the theory of hybrid bond orbitals and simple valence--bond theory have been published in the past few years. Finally, in a series of papers published during the past twelve years, Maksić and co-workers[37-43] employed the theory of hybrid bond orbitals to develop a method (the »iterative-maximum-overlap approximation«) for computing the structural properties of hydrocarbons.

II. THEORY

A. *The Rigorous Calculation of the Bond Strength* S

The strength S of a hybrid bond orbital is defined as the value in the bond direction of the angular part of the bond orbital, normalized to 4π[1,18]. It is a measure of the energy gained through bond formation. The hybrid bond orbitals for a particular molecular system are composed of a linear combination of the spherical harmonics, normalized to 4π (Table I). Which of the various spherical harmonics contribute to a set of hybrid orbitals is determined by the symmetry of the system. The exact bond strength S is calculated by determining the values of the coefficients in the linear combination of spherical harmonics that maximizes a reference orbital in its bond direction, subject to the restraints of normalization and orthogonality[1,18]. For a set of hybrid bond orbitals which are equivalent by geometrical symmetry operations one may employ the Lagrange method of undetermined multipliers to determine the coefficients[1,34].

Z. S. HERMAN AND L. PAULING

TABLE I

The Real Spherical Harmonics (Normalized to 4π)

$l = 0$ $s = 1$

$l = 1$ $p_x = \sqrt{3}\, \sin\Theta\, \cos\phi$

           $p_y = \sqrt{3}\, \sin\Theta\, \sin\phi$

           $p_z = \sqrt{3}\, \cos\Theta$

$l = 2$ $d_{z^2} \quad = \sqrt{5/4}\ (3\cos^2\Theta - 1)$

           $d_{xz} \quad = \sqrt{15}\, \sin\Theta\, \cos\Theta\, \cos\phi$

           $d_{yz} \quad = \sqrt{15}\, \sin\Theta\, \cos\Theta\, \sin\phi$

           $d_{x^2-y^2} = \sqrt{15/4}\, \sin^2\Theta\, \cos 2\phi$

           $d_{xy} \quad = \sqrt{15/4}\, \sin^2\Theta\, \sin 2\phi$

$l = 3$ $f_1 = f_{z(z^2-3r^2)} \quad = \sqrt{7/4}\ (5\cos^3\Theta - 3\cos\Theta)$

           $f_2 = f_{x(5z^2-r^2)} \quad = \sqrt{21/8}\, \sin\Theta\, (5\cos^2\Theta - 1)\, \cos\phi$

           $f_3 = f_{y(5z^2-r^2)} \quad = \sqrt{21/8}\, \sin\Theta\, (5\cos^2\Theta - 1)\, \sin\phi$

           $f_4 = f_{z(x^2-y^2)} \quad = \sqrt{105/4}\, \sin^2\Theta\, \cos\Theta\, \cos 2\phi$

           $f_5 = f_{xyz} \quad = \sqrt{105/4}\, \sin^2\Theta\, \cos\Theta\, \sin 2\phi$

           $f_6 = f_{x(x^2-3y^2)} \quad = \sqrt{35/8}\, \sin^3\Theta\, \cos 3\phi$

           $f_7 = f_{y(3x^2-y^2)} \quad = \sqrt{35/8}\, \sin^3\Theta\, \sin 3\phi$

However, when treating a system composed of different sets of hybrid bond orbitals that are only equivalent within each set, this method leads in general to a series of non-linear, inhomogeneous equations whose solution is quite difficult, if not impossible. In this case, one may proceed by coupling the Lagrange method of undetermined multipliers to the general orthonormalization scheme proposed by Löwdin[44,45]. First one employs the character projection operator to obtain symmetry adapted hybrid orbitals with unknown coefficients for the basis set being considered[3,46,47]. Then one separates within each set the basis orbitals that occur only in one set from those that occur in more than one set. The coefficients of the former are determined using Lagrangian multipliers in the usual way[1]. The latter define a set of reference functions $\{\bar{\varphi}_i\}$. The Lagrange method of undetermined multipliers is then employed to ascertain values of the combination coefficients that maximize each reference function subject to the normalization of each reference function. Finally, the resulting set of normalized reference functions $\{\varphi_i\}$ is orthogonalized according to the matrix prescription[44,45]:

$$\boldsymbol{\psi} = \boldsymbol{\varphi}\, \Delta^{-1/2}\, \mathbf{B} \tag{1}$$

where $\boldsymbol{\psi} = (\psi_1\, \psi_2 \ldots)$ is a row vector composed of the reference hybrid bond orbitals, $\boldsymbol{\varphi} = (\varphi_1\, \varphi_2 \ldots)$ is the vector of the best normalized functions, $\Delta^{-1/2}$ is the positive square root matrix related to the metric matrix Δ, whose elements are

and B is the unitary matrix which leads to a maximum in the weighted-average bond strength of the set $\{\psi_i\}$, the weighting factors being the number of bonding orbitals in each set for which φ_i are representative functions.

For the case of two real reference functions,

$$\Delta^{-1/2} B = (1/2) \begin{pmatrix} X+Y & Y-X \\ Y-X & X+Y \end{pmatrix} \begin{pmatrix} \cos\omega & \sin\omega \\ -\sin\omega & \cos\omega \end{pmatrix} \tag{3}$$

where

$$X = (1 - \langle \varphi_1 | \varphi_2 \rangle)^{-1/2} \tag{4}$$

$$Y = (1 + \langle \varphi_1 | \varphi_2 \rangle^{-1/2} \tag{5}$$

and ω is chosen such that the weighted average bond strength of the set of hybrid bond orbitals $\{\psi_i\}$ defined by equation (1) is a maximum. The details of this approach will be discussed in a forthcoming paper.

B. *The Pair-Defect-Sum Approximation to the Bond Strength*

The problem of rigorously calculating the bond strength for a particular system is, in general, a difficult one and demands the use of a digital computer for solution. In order to avoid this difficulty the pair-defect-approximation to the bond strength was formulated[24,25]. This approximation is based on the equations giving the strength S_0 of two equivalent, orthonormal hybrid bond orbitals that have the maximum strength in directions making the angle α with one another. For sp^3, sp^3d^5, and $sp^3d^5f^7$ hybrid orbitals the equations for the bond strength $S_0(\alpha)$ are given by equations (6), (7) and (8), respectively[24,25]:

$$S_0^{sp}(\alpha) = (0.5 + 1.5x)^{1/2} + (1.5 - 1.5x)^{1/2} \tag{6}$$

$$S_0^{spd}(\alpha) = (3 - 6x + 7.5x^2)^{1/2} + (1.5 + 6x - 7.5x^2)^{1/2} \tag{7}$$

$$S_0^{spdf}(\alpha) = (3 + 15x - 45x^2 + 35x^3)^{1/2} + (5 - 15x + 45x^2 - 35x^3)^{1/2} \tag{8}$$

where $x = \cos^2(\alpha/2)$. For sp^3 hybrid orbitals, the maximum strength $S_{max} = 2$ and occurs at the tetrahedral bond angle 109.47°; and for sp^3d^5 hybrid orbitals, $S_{max} = 3$ at $\alpha = 73.15°$ and $\alpha = 133.62°$; and for $sp^3d^5f^7$ hybrid orbitals, $S_{max} = 4$ at $\alpha = 54.88°$, 100.43°, and 145.37°.[1,25]

The pair-defect-sum approximation S_{approx} to the exact bond strength S of a bond orbital assumes that the defect in the strength (the difference between the maximum value and the value for the orbital) is equal to the sum of the defects, given by equations (6)—(8), corresponding to the several bond angles formed by the orbital with the other bonds in the set. Thus, the approximate bond strength is given by

$$S_{approx} = S_{max} - \Sigma_i [S_{max} - S_0(\alpha_i)] \tag{9}$$

where S_{max} and S_0 are for the appropriate basis set, and the summation is over the angles that a reference orbital makes with all the other orbitals.

The pair-defect-sum approximation was initially subjected to a limited test[25], and then it was systematically tested for an extensive series of systems containing various numbers of hybrid bond orbitals equivalent by geometrical symmetry operations[34]. The approximation was found to be an excellent one in all cases, both with regard to the maximum value of the bond strength and the bond angle or angles for which it occurs. The advantage of the pair-defect-

-sum approximation is that it enables one to compute with a hand calculator within a few minutes the bond strength for virtually any system. Unfortunately, it applies only to orbitals composed of maximum-value basis sets (*e. g., sp^3, sp^3d^5, or $sp^3d^5f^7$* and has not yet been extended to orbitals with arbitrary composition.

<div style="text-align:center">III. RESULTS</div>

A. *Five Hybrid Bond Orbitals Related by a 5-fold Axis of Symmetry (Point Group C_{5v})*

For five bond directions related by a 5-fold axis of symmetry (pentagonal pyramidal coordination), the reference orbital has two orbitals at angle $\alpha_1 =$ $= \arccos (1-2 \sin^2 36° \sin^2 \Theta_0)$ to it and two orbitals at angle $\alpha_2 = \arccos$ $(1-8 \sin^2 36° \sin^2 54° \sin^2 \Theta_0)$ to it, where Θ_0 is the polar angle. For an sp^3d^5 basis set, the reference orbital is given by

$$\psi (\Theta, \phi) = (1/\sqrt{5}) \{[1 + p_z^2 (\Theta_0) + d_{z^2}^2 (\Theta_0)]^{-1/2} \cdot [1 + p_z (\Theta_0)\, p_z (\Theta) + d_{z^2} (\Theta_0)d_{z^2} (\Theta)] +$$

$$+ \sqrt{2}\, [p_x^2 (\Theta_0, 0) + d_{xz}^2 (\Theta_0, 0)]^{-1/2} \cdot [p_x (\Theta_0, 0)\, p_x (\Theta, \phi) + d_{xz} (\Theta_0, 0)\, d_{xz} (\Theta, \phi)] +$$

$$+ \sqrt{2}\, d_{x^2-y^2} (\Theta, \phi)\} \tag{10}$$

The bond strength S for this system is shown as a function of the bond angle α in Figure 1, along with the pair-defect-sum approximation to the bond strength.
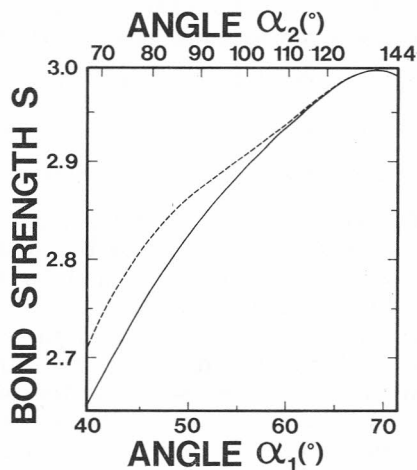

Figure 1. Values of the bond strength as a function of the bond angle for five bond directions related by a 5-fold axis of symmetry (pentagonal pyramid) and with an sp^3d^5 basis set. The exact bond strength S is given by the solid curve, and the dashed curve shows the values calculated by the pair-defect-sum approximation.

The maximum value of the bond strength is given in Table II. For the special case of $\alpha = 72°$ (pentagonal planar coordination), $S = 2.9910$ and ψ has the composition $s^{4/9}p^2d^{23/9}$. It should be noted that a minimum of two d orbitals are required to achieve pentagonal pyramidal coordination for pentacovalent systems.

TABLE II

Maximum Values of the Bond Strength S

System	Basis	S_{max}	Bond Angles	Composition	Strength of Reference Orbitals at S_{max}		
					1	2	3
C_{5v}	sp^3d^5	2.9980 $(2.9980)^a$	$\alpha_1 = 69.83°$ $\alpha_2 = 135.67°$	$s^{0.4485}p^{1.6645}d^{2.8470}$	—	—	—
C_{4v}	sp^3d^5	2.9900 $(2.9900)^a$	$\alpha_1 = 69.19°$ $\alpha_2 = 82.74°$ $\alpha_3 = 138.38°^c$	$s^{0.5965}p^{1.7053}d^{2.6982}$	2.9941 $(2.9951)^a$	2.9890 $(2.9985)^a$	—
		2.9848 $(2.9856)^b$	$\alpha_1 = 123.23°$ $\alpha_2 = 72.52°$ $\alpha_3 = 113.54°$	$s^{0.7731}p^{1.4642}d^{2.7628}$	2.9838 $(2.9852)^a$	2.9850 $(2.9857)^a$	—
	dsp^3	2.5353	$\alpha_1 = 95.21°$ $\alpha_2 = 89.53°$ $\alpha_3 = 169.58°$	$s^1p^3d^1$	1.9659	2.6777	—
C_{3v}	sp^3d^5	2.9522^a	$\alpha_1 = 76.17°$ $\alpha_2 = 103.83°$ $\alpha_3 = 114.47°$ $\alpha_4 = 180°$	—	2.9551^a	2.9118^a	2.9646^a

[a] Pair-defect-sum approximation.

B. *Five Hybrid Bond Orbitals Related by a 4-fold Axis of Symmetry (Point Group C_{4v})*

For five bond directions related by a 4-fold axis of symmetry, there are two reference hybrid orbitals. The first reference orbital, ψ_1, is situated about the z-axis ($\Theta = 0°$) and has four orbitals at angle $\alpha_1 = \Theta_0$ to it. The second reference orbital, ψ_2, lies at polar angle Θ_0, and it has one orbital at angle $\alpha_1 = \Theta_0$ to it, two orbitals at angle $\alpha_2 = \arccos (1 - \sin^2 \Theta_0)$ to it, and one orbital at angle $\alpha_3 = \arccos (1 - 2 \sin^2 \Theta_0)$ to it. The associated reference functions φ_1 and φ_2 are given by

$$\varphi_1 (\Theta) = [1 + p_z^2 (0) + d_{z^2}^2 (0)]^{-1/2} \cdot [1 + p_z (0) p_z (\Theta) + d_{z^2} (0) d_{z^2} (\Theta)] \tag{11}$$

$$\varphi_2 (\Theta) = [1 + p_z^2 (\Theta_0) + d_{z^2}^2 (\Theta_0)]^{-1/2} \cdot [1 + p_z (\Theta_0) p_z (\Theta) + d_{z^2} (\Theta_0) d_{z^2} (\Theta)] \tag{12}$$

Then, according to equations 1 and 3, the reference hybrid bond orbitals are given by

$$\psi_1 (\Theta) = (1/2) \{ \varphi_1 (\Theta) [(X + Y) \cos \omega - (Y - X) \sin \omega] +$$
$$+ \varphi_2 (\Theta) [(Y - X) \cos \omega - (X + Y) \sin \omega] \} \tag{13}$$

$$\psi_2 (\Theta, \phi) = (1/2) \Big((1/2) \{ \varphi_1 (\Theta) [(X + Y) \sin \omega + (Y - X) \cos \omega] +$$
$$+ \varphi_2 (\Theta) [(Y - X) \sin \omega + (X + Y) \cos \omega] \} + d_{x^2-y^2} (\Theta, \phi) +$$
$$+ \sqrt{2} [p_x^2 (\Theta_0, 0) + d_{xz}^2 (\Theta_0, 0)]^{-1/2} \cdot [p_x (\Theta_0, 0) p_x (\Theta, \phi) + d_{xz} (\Theta_0, 0) d_{xz} (\Theta, \phi)] \Big) \tag{14}$$

where

$$X = (1 - \langle \varphi_1 | \varphi_2 \rangle)^{-1/2} \tag{15}$$

$$Y = (1 + \langle \varphi_1 | \varphi_2 \rangle)^{-1/2} \tag{16}$$

and ω is the angle which maximizes the weighted-average of φ_1, and φ_2, i. e. $\varphi_1 + 4 \varphi_2$:

$$\omega = \arctan \left(\frac{4 \varphi_1 (X + Y) + 4 \varphi_2 (Y - X) - \varphi_1 (Y - X) - \varphi_2 (X + Y)}{\varphi_1 (X + Y) + \varphi_2 (Y - X) + 4 \varphi_1 (Y - X) + 4 \varphi_2 (X + Y)} \right) \tag{17}$$

at the respective individual maxima of φ_1 and φ_2, or $\varphi_1 (0)$ and $\varphi_2 (\Theta_0)$.

The bond strength S for this system is shown as a function of the bond angle α_1 in Figure 2, along with the bond strengths S_1 and S_2 of the reference hybrid bond orbitals ψ_1 and ψ_2, as well as the results of the calculation employing the pair-defect-sum approximation. The maximum value of the bond strength is given in Table II. For the special case when the central atom and the four non-axial bonds are coplanar ($\alpha_1 = 90°$), $S = 2.9361$, and the orbitals have the composition $s^{0.8046} p^{2.3665} d^{1.8289}$.

It is possible to achieve a system with five bonds related by a 4-fold axis of symmetry using only one d orbital in an spd basis set. For this special case the reference orbitals are given by
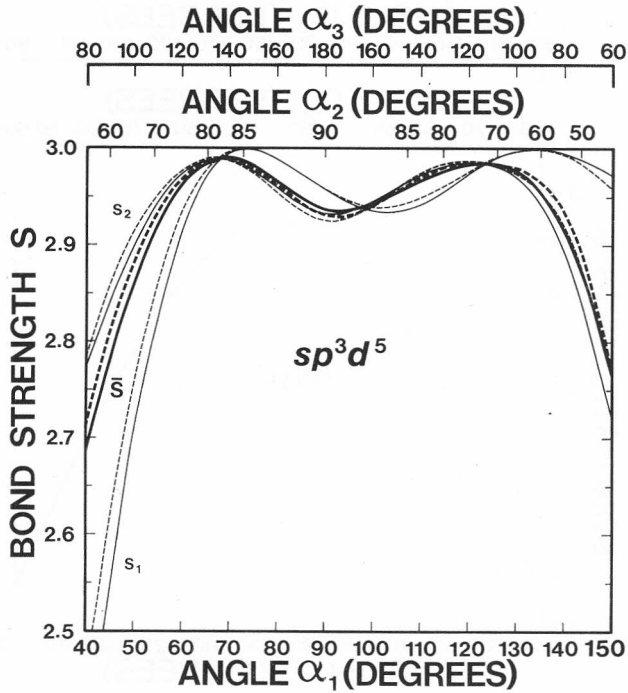
Figure 2. Bond strength as a function of a bond angle for five bond directions related by a 4-fold axis of symmetry and with an $sp^3 d^5$ basis set. The exact and approximate weighted-average bond strengths for the system are given by the thicker curves, and the corresponding strengths S_1 and S_2 for the axial reference orbital ψ_1 and the non-axial reference orbital ψ_2, respectively, are given by the thinner curves. The angles are defined in the text.

and

$$\psi_2 (\Theta, \phi) = (1/2) [a_2 \, s - a_1 \, p_z (\Theta) + d_{x^2-y^2} (\Theta, \phi) + \sqrt{2} \, p_x (\Theta, \phi)] \tag{19}$$

where

$$a_1 = \{[1 - 2 \, p_z (\Theta_0)]^2 + [\sqrt{3} + 2]^2\}^{-1/2} \cdot [1 - 2 \, p_z (\Theta_0)] \tag{20}$$

and

$$a_2 = \{[1 - 2 \, p_z (\Theta_0)]^2 + [\sqrt{3} + 2]^2\}^{-1/2} \cdot [\sqrt{3} + 2] \tag{21}$$

The bond strength S for this case is displayed in Figure 3, along with the bond strengths S_1 and S_2 of ψ_1 and ψ_2, respectively, as a function of the bond angle α_1, and the maximum bond strength is listed in Table II. When $\alpha_1 = 90°$, $S = 2.5271$, and the orbitals have the composition $s^1 p^3 d^1$. As noted previously, it is not possible at present to employ the pair-defect-sum approximation for this limited basis set.
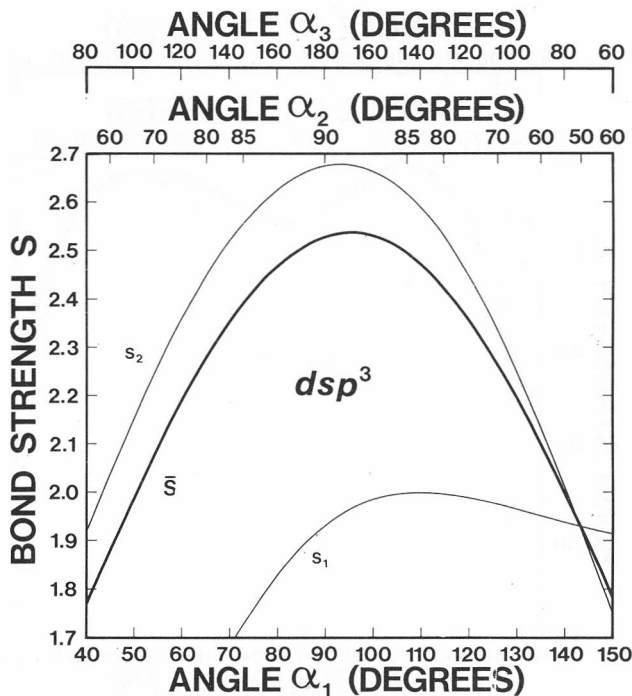
Figure 3. The exact weighted-average and individual bond strengths as a function of bond angle for five bond directions related by a 4-fold axis and with an dsp^3 basis set.

C. Five Hybrid Bond Orbitals Related by a 3-fold Axis of Symmetry (Point Group C_{3v})

For five bond directions related by a 3-fold axis symmetry, there are three reference hybrid bond orbitals, i. e., two non-equivalent axial orbitals, ψ_1 and ψ_2, and a third non-axial orbital ψ_3. Reference orbital ψ_1 lies about the positive z-axis, and it has three orbitals at angle $\alpha_1 = \Theta_0$ to it and one orbital at angle $\alpha_4 = 180°$ to it. Reference orbital ψ_2 lies about the negative z-axis, and it has one orbital at angle $\alpha_4 = 180°$ to it and three orbitals at angle $\alpha_2 = 180° - \Theta_0$ to it. The third reference orbital (ψ_3), which is characteristic of the three equivalent orbitals, has one orbital at angle $\alpha_1 = \Theta_0$ to it, two orbitals at angle $\alpha_3 = \arccos [1 - (3/2) \sin^2 \Theta_0] = 2 \arcsin [(\sqrt{3/2}) \sin \Theta_0]$, and one orbital at angle $\alpha_2 = 180° - \Theta_0$ to it.

For this system, the problem of calculating the bond strength is an exceedingly difficult one (three independent parameters now occur in the three-dimensional unitary (rotation) matrix **B** of equation (1). Owing to the reliability and ease of application of the pair-defect-sum approximation, it should suffice to compute the bond strength in this way. The resulting weighted-average bond strength S_{approx}, along with the individual bond strengths S_1, S_2, and S_3 of the reference hybrid bond orbitals ψ_1, ψ_2, and ψ_3, respectively, is shown in
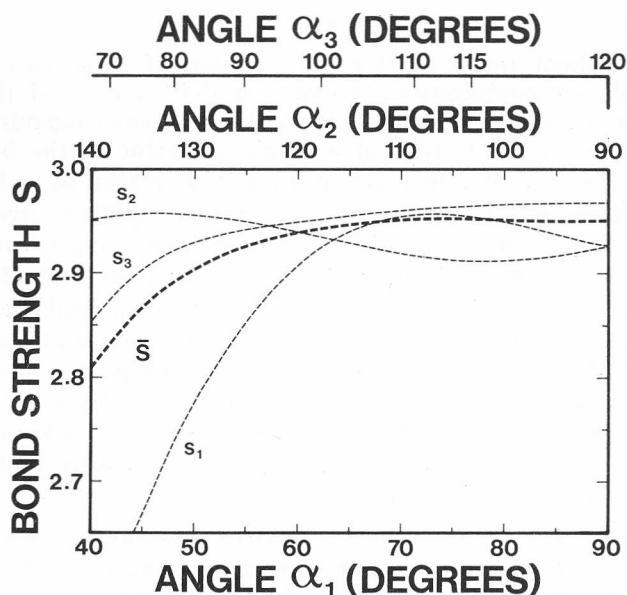
Figure 4. Approximate bond strength as a function of bond angle for five bond directions related by a 3-fold axis of symmetry and with an sp^3d^5 basis set. The weighted-average bond strength is given by the thicker curve, and the strengths S_1, S_2 and S_3 for the two axial reference orbitals ψ_1 and ψ_2 and the non-axial reference orbital ψ_3, respectively, by the thinner curves.

Figure 4, and the maximum value of the bond strength is listed in Table II. For the special case of trigonal bipyramidal coordination ($\alpha_1 = 90°$), the weighted-average bond strength $S_{\text{approx}} = 2.9504$.

This special case of trigonal bipyramidal coordination has also been treated rigorously. The reference hybrid bond orbitals are given by

$$\psi_{\text{axial}}(\Theta) = \psi_1(\Theta) = \psi_2(\Theta) = (1/2)\{[75 + 12\sqrt{30}]^{-1/2} \cdot$$

$$\cdot [(\sqrt{8} + \sqrt{15})s + (\sqrt{12} + \sqrt{40})d_{z^2}(\Theta)] + p_z(\Theta)\} \tag{23}$$

$$\psi_{\text{equatorial}}(\Theta, \phi) = \psi_3(\Theta, \phi) = (1/\sqrt{3})\{[75 + 12\sqrt{30}]^{-1/2} \cdot$$

$$[(\sqrt{12} + \sqrt{40})s - (\sqrt{8} + \sqrt{15})d_{z^2}(\Theta)] +$$

$$+ \sqrt{2}[(2/3)p_x(\Theta, \phi) + \sqrt{5/9}\,d_{x^2-y^2}(\Theta, \phi)]\} \tag{24}$$

The resulting weighted-average bond strength $S = 2.9490$, in excellent agreement with the pair-defect-sum approximation value of 2.9504, and the orbital composition is $s^1p^{17/9}d^{19/9}$.

For pentacovalent bonds in the trigonal bipyramidal coordination geometry and an dsp^3 basis, the reference orbital ψ_{axial} has the same expression as that given by equation (23), and

$$\psi_{\text{equatorial}}(\Theta, \phi) = (1/\sqrt{3})\{[75 + 12\sqrt{30}]^{-1/2} \cdot$$

$$\cdot [(\sqrt{12} + \sqrt{40})s - (\sqrt{8} + \sqrt{15})d_{z^2}(\Theta)] + \sqrt{2}\,p_x(\Theta, \phi)\} \tag{25}$$

The weighted-average bond strength $S = 2.5247$.

IV. DISCUSSION

The most salient result of this investigation of three coordination geometries possible for pentacovalent bonding is that in none of the cases does the situation in which the central atom and the non-axial ligands are coplanar (*i. e.*, polar angle $\Theta_0 = 90°$) occur at a maximum value of the bond strength. However, for the case of five bonding directions related by a 3-fold axis of symmetry (Figure 4), the value of S is rather constant over the range $60° \leq \alpha_1 = \Theta_0 \leq 90°$, indicating that pentacovalent bonding involving this coordination geometry should be characterized by a great deal of non-rigidity. This is consistent with the experimental observation that pentacoordinate systems having trigonal bipyramidal coordination are quite succeptible to distortion[48]. A similar situation prevails for pentacovalent systems having pentagonal prismatic geometries, in that the bond strength S is fairly constant over the range $65° \leq \alpha \leq 72°$ ($66° \leq \Theta_0 \leq 90°$). As far as is known, no pentacoordinate complexes having this geometry have been found, probably because of steric repulsion effects (*vide infra*).

Nevertheless, it is *not* true that S is fairly constant over a large range of bond angles for five bond directions having a 4-fold axis of symmetry. For the sp^3d^5 basis, S has maximum values of 2.9900 and 2.9848 at $\alpha_1 = 69.19°$ ($= \Theta_0$) and $\alpha_1 = 123.23°$, respectively, whereas S has a value of only 2.9371 at $\alpha_1 = 90°$. Owing to steric repulsion effects, the four-ribbed umbrella geometry ($\alpha_1 = 69.19°$) can probably be eliminated from consideration in favor of the four-ribbed, wind-blown umbrella geometry ($\alpha_1 = 123.23°$). This effect is also in evidence for the dsp^3 basis set. For this case S has its maximum value of 2.5353 at $\alpha_1 = 95.21°$ while S equals just 2.5271 at $\alpha_1 = 90°$. These observations are consistent with the experimental evidence that, in pentacordinate systems having this basic geometry, the tetragonal geometry is usually distorted to the extent that the central atom lies above the plane of the four basal ligands.[48]

With regard to the maximum values of the bond strength, it can be seen that, for the sp^3d^5 basis, S is about the same for the C_{5v} and C_{4v} geometries, and it has a considerably lower value for the C_{3v} geometry. However, for most ligands pentagonal pyramidal coordination is rendered less favorable owing to steric repulsion of the ligands. Therefore, all other things being equal, C_{4v} coordination is probably the most favorable one for pentacovalency. Nevertheless, for central atoms having an dsp^3 basis set for bond formation, the C_{4v} and C_{3v} coordination geometries probably lie near each other in energy. Berry[49] pointed out that interconversion of these geometries requires only a bending process.

It is possible that the hypothetical gaseous molecules VH_5, NbH_5, and TaH_5 might have the pentagonal prismatic geometry. Employing the value of $\alpha = 69.83°$, the covalent radius of 0.30 Å for hydrogen, and the pentacovalent radii 1.29 Å, 1.41 Å, and 1.41 Å for vanadium, niobium and tantalum, respectively, one finds H—H distances of 1.83 Å, 1.96 Å, and 1.96 Å for the hypothetical pentagonal prismatic species VH_5, NbH_5, and TaH_5, respectively. These distances are slightly larger than the H—H distance in methane.

V. CONCLUSIONS

The efficacy of the pair-defect-sum approximation in attacking otherwise--difficult problems has been demonstrated. Furthermore, the results of this investigation are consistent with the sparse experimental information available concerning pentacovalent bonding. Further experimental study of the topics discussed herein would be most interesting.

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SAŽETAK

Hibridne orbitale i jačina pentakovalentnog vezanja

Zelek S. Herman i Linus Pauling

Dan je kratak povijesni pregled teorije hibridnih orbitala. Zatim su određene optimalne hibridne orbitale koje daju najčvršće pentakovalentne veze. Razmatrani su slučajevi s trostrukom, četverostrukom i peterostrukom osi prave simetrije. Interesantno je primijetiti da ni u jednom od tih slučajeva nije centralni atom u istoj ravnini s neaksijalnim vezama. Konačno, detaljno su prodiskutirane implikacije ovih rezultata.