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Reliability of the pair-defect-sum approximation for the strength of valence-bond orbitals

(transition metals/lanthanides/actinides/*spd* hybrid orbitals/*spdf* hybrid orbitals)

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ABSTRACT **The pair-defect-sum approximation to the bond strength of a hybrid orbital (angular wave functions only) is compared to the rigorous value as a function of bond angle for seven types of bonding situations, with between three and eight bond directions equivalent by geometrical symmetry operations and with only one independent bond angle. The approximation is seen to be an excellent one in all cases, and the results provide a rationale for the application of this approximation to a variety of problems.**

The quantum mechanical treatment of the electronic structure of molecules has great value. For all except the simplest molecules, it is so difficult to carry out a thorough calculation as essentially to prevent its application. One simplification in the theoretical discussion of the nature of the bonds formed by an atom is to assume that the bond-forming strength of an atomic orbital is proportional to the amount of overlap of the orbital with a bond orbital of an adjacent atom. The amount of overlap increases with increase in the concentration of the bond orbital in the bond direction. A second approximation was made by one of us in 1931. This approximation is based on the knowledge that the radial parts of the atomic orbitals involved in the formation of hybrid bond orbitals are not much different for the different atomic orbitals, so that the assumption that they are the same does not lead to great error. Accordingly attention is focused on the angular distribution of the bond orbitals. The strength, S, of a 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 (1, 2). A number of sets of bond orbitals were discussed in this way (1, 2). Hultgren then attacked the general problem of the best possible sets of sp^3d^5 orbitals (3). The mathematical problem was, however, too difficult to handle before computers had been developed, and Hultgren made a simplifying assumption, the assumption of cylindrical symmetry of the bond orbitals. This assumption led to the erroneous conclusion that sets of more than six bond orbitals would not be well suited to bond formation. Nearly 40 years later the general problem of the best set of nine *spd* bond orbitals was attacked by McClure (4). He found one excellent set of nine hybrid bond orbitals, all with strength close to the maximum possible, 3.

Because of the difficulty in carrying out the calculations rigorously for large sets of orbitals, an approximation was then suggested. This approximation is based on the equations giving the strength S_o of two equivalent 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 $S_o(\alpha)$ have been derived (5, 6)—Eqs. 1, 2, and 3, respectively.

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$$S_o^{sp}(\alpha) = (0.5 + 1.5x)^{1/2} + (1.5 - 1.5x)^{1/2} \quad [1]$$

$$S_o^{spd}(\alpha) = (3 - 6x + 7.5x^2)^{1/2} + (1.5 + 6x - 7.5x^2)^{1/2} \quad [2]$$

$$S_o^{spdf}(\alpha) = (3 + 15x - 45x^2 + 35x^3)^{1/2} + (5 - 15x + 45x^2 - 35x^3)^{1/2}, \quad [3]$$

where $x = \cos^2(\alpha/2)$. For sp^3 hybrid orbitals, the maximum strength S_{max}, 2, is found at the tetrahedral bond angle 109.47°; 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, 6).

The approximation that has been proposed for calculating the strength of hybrid bond orbitals in a set is that the defect in the strength of a bond orbital (the difference between the maximum value and the value for the orbital) is equal to the sum of the defects, given by Eqs. 1–3, corresponding to the several bond angles formed by the orbital with the other bonds in the set (5, 6). Thus, the approximate bond strength S_{approx} is given by

$$S_{approx} = S_{max} - \sum_i [S_{max} - S_o(\alpha_i)], \quad [4]$$

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

This pair-defect-sum approximation has been subjected to a limited test (6). We now have subjected it to an extensive test by comparing the values of the strength given by the approximation with those given by the exact treatment of the seven sets of equivalent, normalized, and mutually orthogonal bond orbitals with between three and eight orbitals equivalent by geometrical symmetry operations and with only one independent bond angle between the various bond directions.

The seven sets are three bond directions related by a 3-fold axis (trigonal pyramid), four bond directions related by a 4-fold axis (tetragonal pyramid), four bond directions toward the corners of a tetragonal bisphenoid, six bond directions toward the corners of a trigonal prism, six bond directions toward the corners of a trigonal antiprism, eight bond directions toward the corners of a tetragonal prism, and eight bond directions toward the corners of a tetragonal antiprism.

For each of these cases, the exact bond strength S has been derived by the rigorous application of the requirements of normalization and orthogonality of the hybrid bond orbitals, followed by variation according to the Lagrange method of undetermined multipliers to evaluate the hybridization coefficients so as to give the maximum value of the bond strengths in the derived directions (1, 6). The spherical harmonics employed in the various basis sets are the following: $s = 1$; $p_x = \sqrt{3}\sin\theta\cos\phi$; $p_y = \sqrt{3}\sin\theta\sin\phi$; $p_z = \sqrt{3}\cos\theta$; $d_{z^2} = \sqrt{5/4}(3\cos^2\theta - 1)$; $d_{xz} = \sqrt{15}\sin\theta\cos\theta\cos\phi$; $d_{yz} = \sqrt{15}\sin\theta\cos\theta\sin\phi$;

$d_{x^2-y^2} = \sqrt{15/4}\,\sin^2\theta\,\cos2\phi$; $d_{xy} = \sqrt{15/4}\,\sin^2\theta\,\sin2\phi$; and

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

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

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

$$f_4 = f_{z(x^2-y^2)} = \sqrt{105/4}\,\sin^2\theta\,\cos\theta\,\cos2\phi,$$

$$f_5 = f_{xyz} = \sqrt{105/4}\,\sin^2\theta\,\cos\theta\,\sin2\phi,$$

$$f_6 = f_{x(x^2-3y^2)} = \sqrt{35/8}\,\sin^3\theta\,\cos3\phi,$$

$$f_7 = f_{y(3x^2-y^2)} = \sqrt{35/8}\,\sin^3\theta\,\sin3\phi.$$

In each case the reference hybrid orbital ψ has been chosen so that it has the maximum allowed value at the polar angle θ_o in the xz plane ($\phi = 0°$).

There are some limitations on the sets that can be formed from a given basis set. For example, if in a set of n equivalent orbitals there is a center of symmetry, the orthogonality requirement leads to the conclusion that the number of even orbitals contributing to the set must be equal to the number of odd orbitals. This theorem leads immediately, for example, to the conclusion that eight equivalent orbitals directed toward the corners of a tetragonal prism cannot be formed by *spd* hybridization because there are only three odd orbitals (the three p orbitals) in the basis set.

Values of the strength as a function of a characteristic bond angle, calculated by the rigorous method, are shown by the solid curves in Figs. 1–7. The dashed curves show the values calculated by the pair-defect-sum approximation (Eq. 4). It is seen that the errors introduced by the approximation are not very great. The maximum values of the exact bond strength are given in Table 1.

In the following list we present the reference hybrid orbital for each case. In addition, the average percent error $\langle\text{Err}\rangle = 100\% \cdot \langle[S - S_{\text{approx}}]/S\rangle$ is presented.

1. Trigonal pyramid (point group C_{3v})

For three bond directions related by a 3-fold axis, the reference orbital has two orbitals at angle $\alpha = 2\arcsin[(\sqrt{3}\sin\theta_o)/2]$ to it. For the various basis sets, the reference function ψ and the average error are given as follows.

sp^3 basis [$\langle\text{Err}\rangle = 1.418\%$ ($40° \le \alpha \le 120°$)]:

$$\psi_{sp}(\theta, \phi) = (1/\sqrt{3})\,\{[1 + p_z^2(\theta_o)]^{-1/2} \cdot [1 + p_z(\theta_o)p_z(\theta)] + \sqrt{2}p_x(\theta, \phi)\}. \quad [5]$$

sp^3d^5 basis [$\langle\text{Err}\rangle = 0.229\%$ ($40° \le \alpha \le 120°$)]:

$$\psi_{spd}(\theta, \phi) = (1/\sqrt{3})\,\{[1 + p_z^2(\theta_o) + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + p_z(\theta_o)p_z(\theta) + d_{z^2}(\theta_o)d_{z^2}(\theta)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0) + d_{x^2-y^2}^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi)]\}. \quad [6]$$

$sp^3d^5f^7$ basis [$\langle\text{Err}\rangle = 0.034\%$ ($40° \le \alpha \le 120°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/\sqrt{3})\,\{[1 + p_z^2(\theta_o) + d_{z^2}^2(\theta_o) + f_1^2(\theta_o) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [1 + p_z(\theta_o)p_z(\theta) + f_1(\theta_o)f_1(\theta) + f_6(\theta_o, 0)f_6(\theta, \phi)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0) + d_{x^2-y^2}^2(\theta_o, 0) + f_2^2(\theta_o, 0) + f_4^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi) + f_4(\theta_o, 0)f_4(\theta, \phi)]\}. \quad [7]$$

For the special case of $\alpha = 120°$, $S_{sp} = 1.9916$ (composition: $s^{1/6}p^{5/6}$), $S_{spd} = 2.9873$ ($s^{0.1667}p^{0.3565}d^{0.4769}$), and $S_{spdf} = 3.9860$ ($s^{0.0769}p^{0.1912}d^{0.2857}f^{0.4462}$) (Fig. 1).

2. Tetragonal pyramid (C_{4v})

For four bond directions related by a 4-fold axis of the first kind, the reference orbital ψ has two orbitals at angle $\alpha_1 = 2$

Table 1. Maximal values of the exact bond strength S

System	Basis	S_{max}	Bond angles	Composition
Trigonal	sp^3	2.0000	α = 109.47°	$s^{1/4}p^{3/4}$
pyramid	sp^3d^5	3.0000	α = 73.15°	$s^{1/9}p^{1/3}d^{5/9}$
	$sp^3d^5f^7$	4.0000	α = 54.88°; α = 100.43°	$s^{1/16}p^{3/16}d^{5/16}f^{7/16}$
Tetragonal	sp^3d^5	2.9946	α_1 = 78.46°; α_2 = 126.86°	$s^{5/36}p^{1/3}d^{19/36}$
pyramid	$sp^3d^5f^7$	3.9900	α_1 = 57.55°; α_2 = 85.81°	$s^{0.0789}p^{0.2042}d^{0.2964}f^{0.4205}$
		3.9827	α_1 = 85.50°; α_2 = 147.47°	$s^{0.0862}p^{0.1896}d^{0.2908}f^{0.4335}$
Tetragonal	sp^3	2.0000	α_1 = 109.47°; α_2 = 109.47°	$s^{1/4}p^{3/4}$
bisphenoid	sp^3d^5	2.9994	α_1 = 71.55°; α_2 = 131.17°	$s^{0.1143}p^{0.3211}d^{0.5646}$
		2.9716	α_1 = 141.21°; α_2 = 96.33°	$s^{0.1603}p^{0.3474}d^{0.4924}$
	$sp^3d^5f^7$	3.9992	α_1 = 53.80°; α_2 = 142.68°	$s^{0.0585}p^{0.1932}d^{0.3060}f^{0.4423}$
		3.9923	α_1 = 109.47°; α_2 = 109.47°	$s^{0.0511}p^{0.2025}d^{0.3375}f^{0.4089}$
Trigonal	sp^3d^5	2.9887	α_1 = 79.01°; α_2 = 85.46°; α_3 = 136.90°	$s^{0.1410}p^{0.3657}d^{0.4932}$
prism	$sp^3d^5f^7$	3.9937	α_1 = 56.86°; α_2 = 113.30°; α_3 = 148.09°	$s^{0.0637}p^{0.1953}d^{0.3318}f^{0.4092}$
		3.9857	α_1 = 100.32°; α_2 = 55.10°; α_3 = 127.37°	$s^{0.0507}p^{0.2203}d^{0.3133}f^{0.4157}$
Trigonal	sp^3d^5	2.9255	α_1 = 78.85°; α_2 = 101.15°	$s^{0.1404}p^{1/2}d^{0.3596}$
antiprism		2.9243	α_1 = 96.42°; α_2 = 83.58°	$s^{0.1569}p^{1/2}d^{0.3431}$
	$sp^3d^5f^7$	3.9526	α_1 = 57.18°; α_2 = 122.82°	$s^{0.0675}p^{0.1806}d^{0.4325}f^{0.3194}$
		3.9536	α_1 = 120°; α_2 = 60°	$s^{0.0741}p^{0.4259}d^{0.1778}f^{0.3222}$
Tetragonal	$sp^3d^5f^7$	3.9380	α_1 = 61.62°; α_2 = 92.82°; α_3 = 87.18°; α_4 = 118.38°	$s^{0.1019}p^{0.1836}d^{0.3981}f^{0.3164}$
prism		3.9368	α_1 = 76.51°; α_2 = 122.24°; α_3 = 57.76°; α_4 = 103.49°	$s^{0.1124}p^{0.1751}d^{0.3877}f^{0.3249}$
Tetragonal	sp^3d^5	2.9884	α_1 = 76.32°; α_2 = 121.80°; α_3 = 72.34°; α_4 = 140.93°	$s^{0.1131}p^{3/8}d^{0.5119}$
antiprism	$sp^3d^5f^7$	3.9881	α_1 = 58.29°; α_2 = 87.06°; α_3 = 100.96°; α_4 = 149.44°	$s^{0.0883}p^{0.1910}d^{0.3124}f^{0.4083}$
		3.9764	α_1 = 85.10°; α_2 = 146.01°; α_3 = 55.85°; α_4 = 137.06°	$s^{0.0739}p^{0.2199}d^{0.2724}f^{0.4338}$

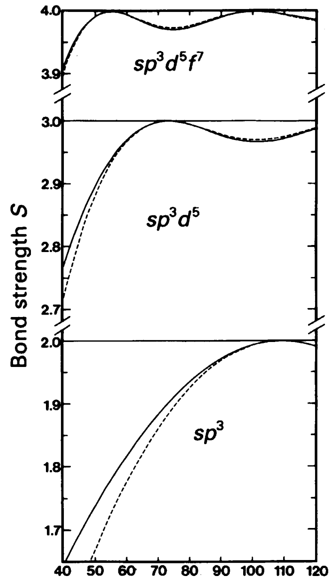

FIG. 1. Values of the bond strength as a function of the bond angle for three bond directions related by a 3-fold axis (trigonal pyramid) for the different possible basis sets. The exact bond strength is given by the solid curve, and the dashed curve shows the values calculated by the pair-defect-sum approximation.

$\arcsin[(\sin\theta_o)/\sqrt{2}]$ to it and one orbital at angle $\alpha_2 = 2\theta_o$ to it.

sp^3d^5 basis [$\langle \mathrm{Err} \rangle = 0.370\%$ ($40° \le \alpha_1 \le 90°$)]:

$$\psi_{spd}(\theta, \phi) = (1/2)\{[1 + p_z^2(\theta_o) + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + p_z(\theta_o)p_z(\theta) + d_{z^2}(\theta_o)d_{z^2}(\theta)] + d_{x^2-y^2}(\theta, \phi) + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi)]\}. \quad [8]$$

$sp^3d^5f^7$ basis [$\langle \mathrm{Err} \rangle = 0.102\%$ ($40° \le \alpha_1 \le 90°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/2)\{[1 + p_z^2(\theta_o) + d_{z^2}^2(\theta_o) + f_1^2(\theta_o)]^{-1/2} \cdot [1 + p_z(\theta_o)p_z(\theta) + d_{z^2}(\theta_o)d_{z^2}(\theta) + f_1(\theta_o)f_1(\theta)] + [d_{x^2-y^2}^2(\theta_o, 0) + f_4^2(\theta, 0)]^{-1/2} \cdot [d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + f_4(\theta_o, 0)f_4(\theta, \phi)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0) + f_2^2(\theta_o, 0) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi) + f_4(\theta_o, 0)f_4(\theta, \phi)]\}. \quad [9]$$

A square planar system occurs for $\alpha_1 = 90°$; in this situation, $S^{spd} = 2.9430$ ($s^{1/9}p^{1/2}d^{7/18}$) and $S^{spdf} = 3.9543$ ($s^{1/9}p^{3/20}d^{7/18}f^{7/20}$) (Fig. 2). The former value is the same as that obtained by Kuhn (7).

3. Tetragonal bisphenoid (D_{2d})

For four bond directions related by a 4-fold axis of the second kind, the reference orbital has one orbital at angle $\alpha_1 = 2\theta_o$ to it and two orbitals at $\alpha_2 = \arccos[1/(\tan^2\theta_o + 1)]$ to it.

sp^3 basis [$\langle \mathrm{Err} \rangle = 1.661\%$ ($40° \le \alpha_1 \le 180°$)]:

$$\psi_{sp}(\theta, \phi) = (1/2)\,[s + p_z(\theta) + \sqrt{2}p_x(\theta, \phi)]. \quad [10]$$

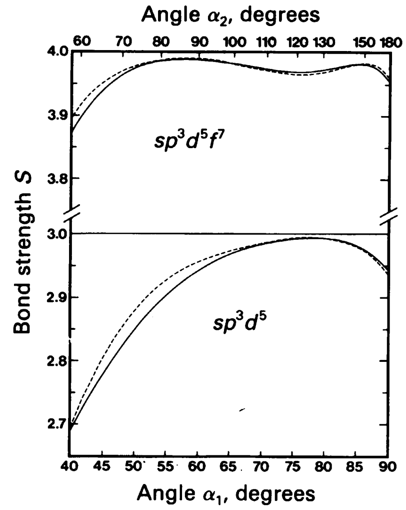

FIG. 2. Bond strength as a function of a bond angle for four bond directions related by a 4-fold axis of the first kind (tetragonal pyramid). The angles are defined in the text.

sp^3d^5 basis [$\langle \mathrm{Err} \rangle = 0.175\%$ ($40° \le \alpha_1 \le 180°$)]:

$$\psi_{spd}(\theta, \phi) = (1/2)\{[1 + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + [p_z^2(\theta_o) + d_{x^2-y^2}^2(\theta_o, 0)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi)]\}. \quad [11]$$

$sp^3d^5f^7$ basis [$\langle \mathrm{Err} \rangle = 0.038\%$ ($40° \le \alpha_1 \le 180°$)].

$$\psi_{spdf}(\theta, \phi) = (1/2)\{[1 + d_{z^2}^2(\theta_o) + f_4^2(\theta_o, 0)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta_o) + f_4(\theta_o, 0)f_4(\theta, \phi)] + [p_z^2(\theta_o) + d_{x^2-y^2}^2(\theta_o, 0) + f_1^2(\theta_o)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + f_1(\theta_o)f_1(\theta)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0) + f_2^2(\theta_o, 0) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi) + f_6(\theta_o, 0)f_6(\theta, \phi)]\}. \quad [12]$$

For the sp^3 basis set, the hybrid orbitals are completely determined by symmetry, and S_{sp} has its maximum value of 2 at $\alpha_1 = 109.47°$ and $S_{sp} = 1.7247$ at $\alpha_1 = 180°$ (square planar) (Fig. 3). In the tetrahedral geometry, the results for the other basis sets are $S_{spd} = 2.9495$ ($s^{1/4}p^{9/32}d^{15/32}$), in agreement with Pauling (1) and with Kuhn (7), and $S_{spdf} = 3.9923$ ($s^{0.0511}p^{0.2025}d^{0.3375}f^{0.4089}$). The other special case, that of square planar, has already been mentioned under the tetragonal pyramid. It is worth noting that neither for sp^3d^5 nor for $sp^3d^5f^7$ basis sets does S have its absolute maximum for either the tetrahedral or square planar geometries; indeed, S_{spd} and S_{spdf} are local minima for the square planar system and S_{spd} is a local minimum for the case of the tetrahedron.

4. Trigonal prism (D_{3h})

In this situation the reference orbital has two orbitals at angle $\alpha_1 = 2\arcsin[(\sqrt{3}\sin\theta_o)/2] = \arccos[1 - (3/2)\sin^2\theta_o]$ to it, one orbital at angle $\alpha_2 = \arccos[1 - 2\cos^2\theta_o]$, and two orbitals at

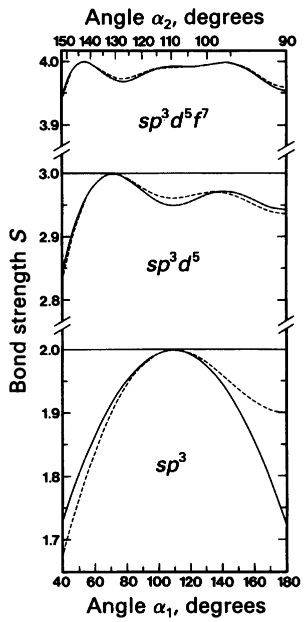

FIG. 3. Bond strength as a function of bond angle for four bond directions related by a 4-fold axis of the second kind (tetragonal bisphenoid).

angle $\alpha_3 = \arccos[1 - (3 + \cos^2\theta_o)/2]$ to it (Fig. 4).

sp^3d^5 basis [$\langle \text{Err} \rangle = 0.163\%$ ($40° \le \alpha_1 \le 120°$)]:

$$\psi_{spd}(\theta, \phi) = (1/\sqrt{6})\{[1 + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + p_z(\theta) + \sqrt{2}d_{xz}(\theta, \phi) + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{x^2-y^2}^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi)]\}. \quad [13]$$

$sp^3d^5f^7$ basis [$\langle \text{Err} \rangle = 0.084\%$ ($40° \le \alpha_1 \le 120°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/\sqrt{6})\,\{[1 + d_{z^2}^2(\theta_o) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta) + f_6(\theta_o, 0)f_6(\theta, \phi)] + [p_z^2(\theta_o) + f_1^2(\theta_o)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + f_1(\theta_o)f_1(\theta)] + \sqrt{2}\,[p_x^2(\theta_o, 0) + d_{x^2-y^2}^2(\theta_o, 0) + f_2^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi)] + \sqrt{2}\,[d_{xz}^2(\theta_o, 0) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + f_6(\theta_o, 0)f_6(\theta, \phi)]\}. \quad [14]$$

5. Trigonal antiprism (D_{3d})

For the trigonal antiprism, the reference orbital has two orbitals at angle $\alpha_1 = 2\arcsin[(\sqrt{3}\sin\theta_o)/2]$ to it, two orbitals at angle $\alpha_2 = 180° - \alpha_1$, and one orbital at angle $\alpha_3 = 180°$ to it.

sp^3d^5 basis [$\langle \text{Err} \rangle = 0.735\%$ ($40° \le \alpha_1 \le 120°$)]:

$$\psi_{spd}(\theta, \phi) = (1/\sqrt{6})\,\{[1 + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + p_z(\theta) + \sqrt{2}p_x(\theta, \phi) + \sqrt{2}\,[d_{x^2-y^2}^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0)]^{-1/2} \cdot [d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi)]\}. \quad [15]$$

$sp^3d^5f^7$ basis [$\langle \text{Err} \rangle = 0.187\%$ ($40° \le \alpha_1 \le 120°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/\sqrt{6})\,\{[1 + d_{z^2}^2(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + [p_z^2(\theta_o) + f_1^2(\theta_o) + f_6^2(\theta_o, 0)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + f_1(\theta_o)f_1(\theta) + f_6(\theta_o, 0)f_6(\theta, \phi)] + \sqrt{2}\,[p_x^2(\phi_o, 0) + f_2^2(\theta_o, 0) + f_4^2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi) + f_4(\theta_o, 0)f_4(\theta, \phi)] + \sqrt{2}\,[d_{x^2-y^2}^2(\theta_o, 0) + d_{xz}^2(\theta_o, 0)]^{-1/2} \cdot [d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi)]\}. \quad [16]$$

The special case of the regular octahedron occurs for $\alpha_1 = 90°$; here $S_{spd} = 2.9240$ ($s^{1/6}p^{1/2}d^{1/3}$), in agreement with the result of 1931 (1), and $S_{spdf} = 3.9353$ ($s^{1/6}p^{3/20}d^{1/3}f^{7/20}$). It is interesting to note that for both basis sets, S has a local minimum for the octahedron (Fig. 5).

6. Tetragonal prism (D_{4h})

In this situation the reference orbital has two orbitals at angle $\alpha_1 = \arccos(\cos^2\theta_o) = \arcsin[(\sin\theta_o)/\sqrt{2}]$ to it, one orbital at

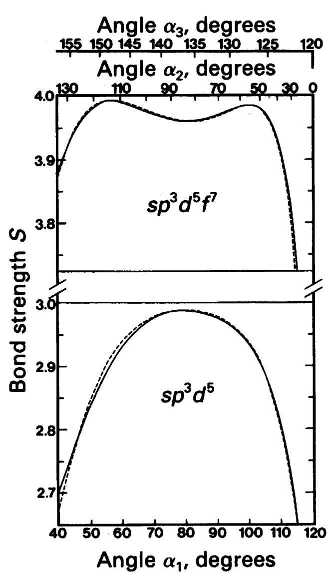

FIG. 4. Bond strength as a function of bond angle for six bond directions at the corners of a trigonal prism.

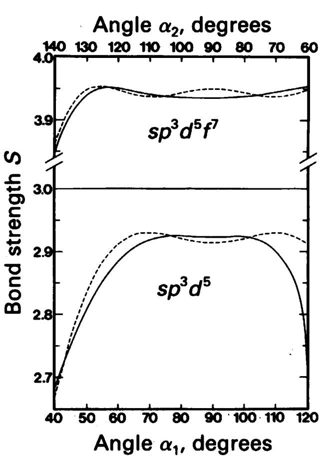

FIG. 5. Bond strength as a function of bond angle for six bond directions at the corners of a trigonal antiprism.

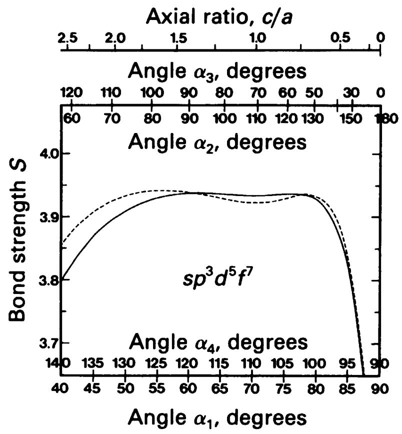

FIG. 6. Bond strength as a function of bond angle for eight bond directions at the corners of a tetragonal prism. The axial ratio c/a is defined such that a is the side of either of the squares and c is the distance between the planes formed by each square.

angle $\alpha_2 = 2\theta_o$, one at angle $\alpha_3 = 180° - \alpha_2$, two at angle $\alpha_4 = 180° - \alpha_1$, and one orbital at angle $\alpha_5 = 180°$ to it. Because the eight corners of the tetrahedral prism have a center of symmetry, only the $sp^3d^5f^7$ basis set is possible.

$sp^3d^5f^7$ basis [$\langle \text{Err} \rangle = 0.430\%$ ($40° \leq \alpha_1 \leq 90°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/\sqrt{8})\{[1 + d^2_{z^2}(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + [p^2_z(\theta_o) + f^2_1(\theta_o)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + f_1(\theta_o)f_1(\theta)] + \sqrt{2}\,[p^2_x(\theta_o, 0) + f^2_2(\theta_o, 0) + f^2_6(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi) + f_6(\theta_o, 0)f_6(\theta, \phi)] + d_{x^2-y^2}(\theta, \phi) + f_4(\theta, \phi) + \sqrt{2}d_{xz}(\theta, \phi)\}. \quad [17]$$

The special case of the cube occurs when $\alpha_1 = 70.53°$ (the supplement of the tetrahedral angle); in this situation $S_{spdf} = 3.9339$ ($s^{1/8}p^{81/440}d^{3/8}f^{139/440}$) and corresponds to a local minimum, although the curves are rather flat over a large region (Fig. 6).

7. Tetragonal antiprism (D_{4d})

For the tetragonal antiprism, the reference orbital has two orbitals at angle $\alpha_1 = 2\arcsin[(\sin\theta_o)/\sqrt{2}]$, one orbital at angle $\alpha_2 = 2\theta_o$, two at angle $\alpha_3 = \arccos(1/\sqrt{2})[1 - (\sqrt{2} + 1)\cos^2\theta_o]$, and two orbitals at $\alpha_4 = \arccos(-1/\sqrt{2})[1 + (\sqrt{2} - 1)\cos^2\theta_o]$ to it.

sp^3d^5 basis [$\langle \text{Err} \rangle = 0.995\%$ ($40° \leq \alpha_1 \leq 90°$)]:

$$\psi_{spd}(\theta, \phi) = (1/\sqrt{8})\{[1 + d^2_{z^2}(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + p_z(\theta) + \sqrt{2}p_x(\theta, \phi) + \sqrt{2}d_{x^2-y^2}(\theta, \phi) + \sqrt{2}d_{xz}(\theta, \phi)\}. \quad [18]$$

$sp^3d^5f^7$ basis [$\langle \text{Err} \rangle = 0.230\%$ ($40° \leq \alpha_1 \leq 90°$)]:

$$\psi_{spdf}(\theta, \phi) = (1/\sqrt{8})\{[1 + d^2_{z^2}(\theta_o)]^{-1/2} \cdot [1 + d_{z^2}(\theta_o)d_{z^2}(\theta)] + [p^2_z(\theta_o) + f^2_1(\theta_o)]^{-1/2} \cdot [p_z(\theta_o)p_z(\theta) + f_1(\theta_o)f_1(\theta)] + \sqrt{2}\,[p^2_x(\theta_o, 0) + f^2_2(\theta_o, 0)]^{-1/2} \cdot [p_x(\theta_o, 0)p_x(\theta, \phi) + f_2(\theta_o, 0)f_2(\theta, \phi)] + \sqrt{2}\,[d^2_{x^2-y^2}(\theta_o, 0) + f^2_4(\theta_o, 0)]^{-1/2} \cdot [d_{x^2-y^2}(\theta_o, 0)d_{x^2-y^2}(\theta, \phi) + f_4(\theta_o, 0)f_4(\theta, \phi)] + \sqrt{2}\,[d^2_{xz}(\theta_o, 0) + f^2_6(\theta_o, 0)]^{-1/2} \cdot [d_{xz}(\theta_o, 0)d_{xz}(\theta, \phi) + f_6(\theta_o, 0)f_6(\theta, \phi)]\}. \quad [19]$$

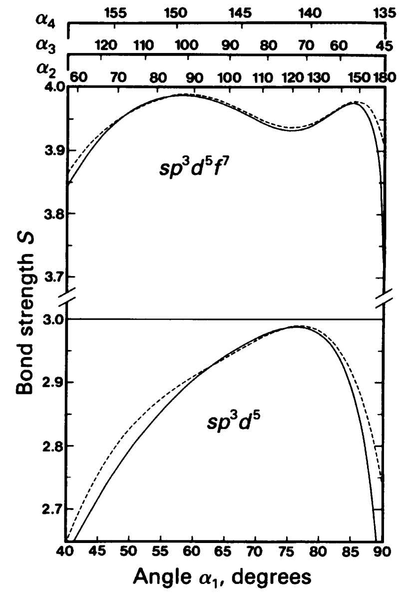

FIG. 7. Bond strength as a function of bond angle for eight bond directions at the corners of a tetragonal antiprism.

For the sp^3d^5 basis, the hybrid orbitals have the general composition $s^{x/8}p^{3/8}d^{(5-x)/8}$. The absolute maximum of $S_{spd} = 2.9884$ occurs at $\alpha_1 = 76.32°$ (Fig. 7)—that is, when the corners of the tetragonal antiprism are at an angle of 60.90° with the tetragonal axis, in agreement with Racah's result for the best set of eight equivalent *spd* hybrid orbitals (8).

From Figs. 1–7, it is seen that the pair-defect-sum approximation to the bond strength seems to be an excellent one over the range of chemically significant bond angles. The difference between the rigorous bond strength and the approximate one is in all cases small. Moreover, the maxima in S as predicted by the pair-defect-sum approximation are near to or coincident with the exact maxima. For a given symmetry, the larger the basis set the better is the approximation, and the agreement between S and S_{approx} is better for systems with a smaller number of bonds, as expected.

In view of the efficacy of the pair-defect-sum approximation, we are proceeding with its application to some problems of interest, especially the problem of the best set of nine equivalent *spd* orbitals.

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