The Nature of Bond Orbitals in Quadricovalent Complexes of Transition Elements

Hans Kuhn

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taining, expanding, and solving the secular determinants) were carried out numerically.

The force constants given in Table VII were evaluated from known frequencies of ethane, propane, as shown in the table. The frequencies calculated from these force constants, which are discussed in Sections III and IV are:

Isobutane:	A_1	776 cm^{-1}
		(434)
	E	1034
		369
Neopentane:	A_1	729 cm^{-1}
	E	230
	T_2	983
		422

APPENDIX B

HCC Bending Force Constant Calculations on Propane and Isobutane

In the models used, the CH_3 groups were considered as point masses, but the secondary and tertiary hydrogens were included in the calculations. The methods used were the same as those described in Appendix A, with the additional simplification that the CH stretching force constants were set equal to infinity and the CH stretching vibrations were separated from the others and subsequently ignored, according to the procedure given by Wilson.[7]

In order to obtain suitable force constants for use with these models, calculations were made under similar assumptions on methane and ethane. The force constants used, and their sources, are given in Table VIII. The calculated frequencies, which are discussed in Sections III and IV, are:

Propane:	A_1	898 cm^{-1} (C—C stretching)
		1467 (HCH bending)
		427 (C—C—C bending)
	A_2	1175 (CH$_2$ twisting)
	B_1	998 (C—C stretching)
		1205 (CH$_2$ wagging)
	B_2	761 (CH$_2$ rocking)
Isobutane:	A_1	821 cm^{-1} (C—C stretching)
		571 (C—C—C bending)
	E	994 (C—C stretching)
		319 (C—C—C bending)
		1113 (CH wagging)

The Nature of Bond Orbitals in Quadricovalent Complexes of Transition Elements*

HANS KUHN**

Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California

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In quadricovalent complexes of transition elements (Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}, Ag^{II}, Cu^{II}) the central atom uses four s or d orbitals of its outer shell for unshared electron pairs and two s or d and two p orbitals for bond formation. The problem here is to find the strongest possible four hybrid bond orbitals obtained by combining the two $s-d$ and the two p orbitals available for bond formation. The strongest bond orbitals thus obtained are directed from the middle towards the four corners of a square, as it is expected from experimental evidence; they are composed of 4/9 s, 14/9 d, and two p orbitals, the strength being 2.943. These strongest possible orbitals are presumably used in complex of Ni^{II}, Pt^{II}, Au^{III}, and Cu^{II}, but probably not in complexes of Pd^{II} and Ag^{II}; in the latter two cases there must be assumed square bond orbitals of composition $s^n d^{2-n} p^2$ with n somewhere between 1 and 4/9, i.e., orbitals of character between that of the strongest square bond orbitals of composition $s^{4/9} d^{14/9} p^2$ mentioned above and that of sdp^2 square orbitals discovered by Pauling.

1. INTRODUCTION

THE problem of directed valence was first developed by Pauling[1] and Slater.[2] Pauling formulated a very simple method of discussing the bond-forming power of an atomic bond orbital. The fundamental assumption of this method is that in the case of bond orbitals with the same or nearly the same radial part of the wave function the magnitude of the angular part of a bond along the bond axis (that is, in the direction of the ligand) is a measure of its relative bond-forming power.

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[1] L. Pauling, J. Am. Chem. Soc. 53, 1367 (1931); The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1945), second edition.
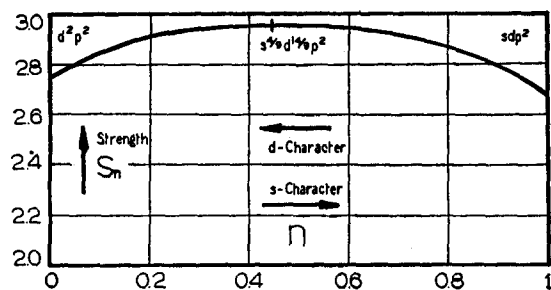[2] J. C. Slater, Phys. Rev. 37, 481 (1931).

FIG. 1. Square bond orbitals. Plot of the strength, S_n, against the amount, n, of s orbitals involved. As there are exactly two p orbitals involved in each square arrangement, the amount of d orbitals is $2-n$, the arrangement thus being $s^n d^{2-n} p^2$.

The bond-forming power or strength S of an s orbital defined in this way is 1, that of a p orbital $\sqrt{3}$, and that of the best d orbital $(5)^{\frac{1}{2}}$.

Pauling has shown that it is possible, by combining s and p or s, p, and d orbitals, to obtain a number of strong bond orbitals (i.e., orbitals with large S). For example, he has found combinations of s and p orbitals which are directed towards the corners of a tetrahedron, combinations of s, p, and d orbitals which are directed toward the corners of a square, and other combinations which are directed towards the corners of an octahedron.

An important result of Pauling's approach is that the four sp orbitals in the directions of the corners of a regular tetrahedron are the strongest possible combinations of s and p orbitals. Thus the tetrahedral valence of carbon and similar elements has found a simple explanation.

In contrast to carbon are the B group elements such as Ni^{II}, Pd^{II}, Pt^{II}, Cu^{II}, and Au^{III}, surrounded by four electronegative atoms generally in a square, and not tetrahedral, arrangement. Pauling has shown that four rather strong bond orbitals with strength $S=2.694$ can be constructed for this square arrangement by hybridization of one s, one d, and two p orbitals.

The question as to whether or not the square bond orbitals discussed by Pauling are the strongest possible four hybrid orbitals has not before been answered. We may think of the possibility of constructing four stronger spd orbitals than the square orbitals; it must be decided whether or not the concept of bond strength enables us to exclude other arrangements as

less stable, such as a tetrahedral or a tetragonal pyramidal arrangement.

2. ELECTRONIC STRUCTURE AND BOND ARRANGEMENT OF QUADRICOVALENT COMPLEXES OF TRANSITION ELEMENTS

a. Square Complexes of Ni^{II}, Pt^{II}, and Au^{III}

Let us look at a covalent complex of bivalent nickel, such as the nickel cyanide ion $[Ni(CN)_4]^{--}$. The twenty-six electrons of Ni^{II} can be placed in the following way: 18 electrons can be placed in the $1s$, $2s$, three $2p$, $3s$, and three $3p$ orbitals; for the other eight electrons six orbitals, namely, the five $3d$ orbitals and the almost equally stable $4s$ orbital, are available, and four of these orbitals may be occupied by electron pairs.[3]

This leaves available for use in bond formation two orbitals of the $3d$–$4s$ shell as well as the three $4p$ orbitals, which are somewhat less stable than the $3d$ and $4s$ orbitals.[4, 5] As four bonds are to be formed, the smallest possible amount of unstable $4p$ orbitals, namely two, should be used. We are left with the problem of determining the geometric arrangement of the four strongest spd hybrid orbitals that can be formed from two p and two s–d orbitals and that are, at the same time, orthogonal to four orbitals with pure $4s$ and $3d$ character (these orbitals being filled with eight electrons of the nickel shell) and to a pure p orbital (this orbital being empty).

For this purpose we shall discuss several geometrical arrangements of four spd bond orbitals, and we shall find that of all arrangements of equivalent orbitals only square arrangements have, in fact, the property stated above of being orthogonal to four s–d orbitals and one p orbital. In Fig. 1 the strength, S_n, of these orbitals as ordinate is plotted against the amount, n, of involved s orbital as abscissa. The square orbitals

[3] The nearly equal stability of $3d$ and $4s$ follows from the position of atomic spectral terms in nickel. The ground state of nickel is a ^3F state corresponding to a configuration $3d^8 4s^2$; the lowest excited state ^3D, corresponding to a structure $3d^9 4s$, is only 0.58 kcal./mole above the ground state (see reference 4). As this energy difference is small compared to any covalent bond energy, it can be neglected in our treatment and $4s$ and $3d$ can be regarded as equally stable.

[4] The difference in stability of $4s$ and $4p$ orbitals may be seen from the spectral terms of nickel. The $^3P°$ term corresponding to the electronic structure $3d^9 4p$ is 81 kcal./mole above the state $3d^9 4s$ ^3D (see reference 5).

[5] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, New York, 1932).

that must be assumed to be actually used in covalent complexes of bivalent nickel are the orbitals with maximum strength. These orbitals are composed of 0.44 s, 1.56 d, and 2.00 p orbitals, the strength of each orbital being 2.943.

These strongest square orbitals are presumably also used in covalent complexes of Pt^{II} and Au^{III}. There is the same number of electrons involved in the outmost $5d$–$6s$ shell of Pt^{II} and Au^{III} as in the $3d$–$4s$ shell of Ni^{II} and furthermore it can be assumed[6] that the $5d$ and $6s$ orbitals are nearly equal in stability, as are $3d$ and $4s$ in nickel; therefore, the same discussion is applicable.

b. Complexes of Pd^{II}

A somewhat different case is found in square complexes of Pd^{II}. The $4d$ and $5s$ orbitals in Pd cannot be assumed as equally stable. If we place 36 of the 44 electrons of Pd^{II} in the inner shells and the other 8 electrons in four of the five $4d$ orbitals, we obtain a state which is, by about 50 kcal./mole, more stable than the state containing the four electron pairs in the $5s$ and in three of the five $4d$ orbitals.[7] In bond formation, hence, there will be a tendency to use as much of the stable $4d$ orbitals as possible for unshared pairs, leaving the less stable $5s$ and $5p$ as well as one of the $4d$ orbitals for bond formation; this tendency by itself would lead to the sp^2d square arrangement found by Pauling.[1] On the other hand, there will be, as in the cases discussed above, a tendency to use the strongest possible bond orbitals, i.e., the $s^{0.44}d^{1.56}p^2$ square bond orbitals. In consequence a compromise will be reached; the bond orbitals will utilize less than

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[6] From the atomic spectra of platinum it can be seen (see reference 4) that the excited state $5d^96s$ ^3D is only 2.35 kcal./mole above the ground state $5d^86s^2$ ^3F.

The difference in stability between $6s$ and $6p$ orbitals in Pt may be of interest. The state $5d^96p$ ^3P is not known in platinum, but it can be estimated that this state is, as in the case of nickel, about 80–90 kcal./mole less stable than the state $5d^96s$ ^3D. (This is seen in the following way: the energy difference between the d^9s ^3D and the d^9p ^3P states in the sequence Ni, Cu^{+1}, Zn^{+2} are 81, 126, 170 kcal./mole, respectively; the corresponding energy values for Au^{+1} and Hg^{+2} are 137 and 173 kcal./mole, respectively (see reference 4); the value in the case of Pt, the element next to the left of Au in the periodic table, is thus found by extrapolation to be about 90 kcal./mole.)

[7] This can be concluded from the atomic spectral terms of Pd. The energy difference between the state $4d^95s$ ^3D and the higher state $4d^85s^2$ ^3F is 52.8 kcal./mole in Pd. (See reference 4.)

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one and more than 0.44 s orbital; we will thus have $s^nd^{2-n}p^2$ square bond orbitals with n somewhere between 1 and 0.44 (see Fig. 1).

The value of n in a given case can be found by the following treatment:

We shall first assume that sp^2d square orbitals are used for bond formation, then we shall replace these orbitals by $s^np^2d^{2-n}$ bond orbitals, n being arbitrary within the limits 0 and 1. The energy difference which is involved in this replacement produces the sum of two parts.

On one hand, the strength of the bond orbitals and therefore the covalent bond energy is changed. Let us denote by $W_{n=1}$ the energy of a bond between the central atom and one of its ligands in the case where the sp^2d square orbitals of strength $S_{n=1} = 2.694$ are used in bond formation. The bond energy that has to be assumed in case that the central atom uses $s^np^2d^{2-n}$ bond orbitals of strength S_n is then equal to $W_n = W_{n=1} \cdot (S_n^2/S_{n=1}^2)$. This follows from a theorem by Pauling, according to which the energy of a bond is proportional to the product of the squares of the strengths of the orbitals of the two atoms involved. Hence, the change of bond energy in the replacement that we are considering (formation of four bonds involving $s^np^2d^{2-n}$ square orbitals instead of bonds involving sp^2d orbitals) is equal to $4W_{n=1}((S_n^2/S_{n=1}^2) - 1)$.

On the other hand, the electronic energy is changed in the replacement under consideration. At first, when sp^2d orbitals are used in bond formation no unstable s orbital is used for unshared pairs. However, when $s^np^2d^{2-n}$ bond orbitals are used, an amount $(1-n)$ of an s orbital is needed for unshared pairs. The interaction energy of a shared pair is in the case of a pure covalent bond the same as that of a single unshared electron;[1] therefore, the energy required for the interchange of $(1-n)$ shared pairs and $(1-n)$ unshared pairs between s and d orbitals is equal to $(1-n)\Delta E$, ΔE being the $s-d$ separation energy, i.e., the energy required for the transport of one electron from the d into the less stable s orbital. Assuming, however, that there are not pure covalent bonds between the central atom and its ligands but bonds with, say, 100-P percent ionic character (the attached atoms being more electronegative than the central atom), the interaction energy of a shared pair with the central atom is equal to that of only P percent of a single electron. The energy required for the interchange of a shared and an unshared pair between s and d orbitals is thus equal to $(2-P/100)\Delta E$ and the energy required for interchanging $(1-n)$ shared and unshared pairs equal to $(1-n)(2-P/100)\Delta E$.

Therefore, the total energy increase ΔU in the replacement under consideration is given by

$$\Delta U = -4W_{n=1}((S_n^2/S_{n=0}^2) - 1) + \Delta E(1-n)(2-P/100).$$

The n value actually used in bond orbital formation is obtained by minimizing ΔU in respect to n. We obtain:

$$(2-P/100)(\Delta E/W_{n=1}) = -(8/S_{n=0}^2)S_n(dS_n/dn).$$

By substituting S_n from Eqs. (10) and (10a) mentioned later we obtain the following values of n for various values

of $\Delta E / W_{n-1} \times (2 - P/100)$:

$(\Delta E / W_{n-1})(2 - P/100)$	n
0.0	4/9
0.27	5/9
0.58	6/9
1.0	7/9
1.8	8/9
∞	1

The bond energy of a single bond in complexes of transition elements may be of the order of 60 to 100 kcal./mole, and, according to Pauling,[8] these bonds are in most cases about 50 percent covalent in character, P thus being about equal to 50; furthermore, the s–d separation energy ΔE in the case of palladium is 50 kcal./mole, as has been mentioned above; the expression $\Delta E / W_{n-1}(2 - P/100)$ hence will be between 0.7 and 1.4; therefore, n probably lies between 2/3 and 8/9 in palladium complexes.

c. Complexes of Cu^{II} and Ag^{II}

In bivalent copper conditions are similar to those in bivalent nickel. Bivalent copper has, however, one electron more than bivalent nickel; we might at first think that this electron would occupy the fifth $3d$ or the about equally stable $4s$ orbital, making it unavailable for bond formation; this would leave available one $3d$–$4s$ and three $4p$ orbitals for bond formation. However, as has been pointed out by Pauling,[1] placing the unshared electron in the third $4p$ orbital (or in a $4s4p3d$ hybrid orbital) and using the residual four orbitals for bond formation involves no loss of energy by the copper atom. Each of the five orbitals under discussion (two $4s$–$3d$ orbitals and three $4p$ orbitals) is occupied either by a shared pair or by the single unshared electron in either formulation, and the interaction energy of a shared pair with the copper atom is the same as that of a single unshared electron.[9]

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[8] L. Pauling, *The Valences of Transition Elements* (Victor Henri Memorial Volume, Liège, 1947).

[9] In Section 2b we have seen that the interaction energy of a shared pair with the central atom is only in the case of pure covalent bonds equal to that of a single unshared electron, and that these energies are somewhat different in the case of covalent bonds partially ionic in character. A consideration similar to that given in Section 2b, the details of which are omitted, has shown that the difference of these two interaction energies is in any reasonable case too small for effecting a change of the nature of the most stable bond orbitals, and shall be neglected here for reason of simplicity.

These considerations leave us with the problem of determining the geometric arrangement of the four strongest spd hybrid orbitals that are orthogonal to four orbitals with pure s–d character (these orbitals being filled with unshared pairs) and to an orbital of arbitrary composition in s, p, and d (this orbital being filled with the single unshared electron).

We shall find in the following treatment that the best possible orbitals that can be constructed under this condition are again the best square bond orbitals with strength 2.943 described above. These orbitals thus must be assumed for Cu^{II} complexes, which are in fact found to have a square arrangement.

Quadricovalent complexes of bivalent silver, like those of bivalent copper, are found to be coplanar. The same number of electrons are involved in the outer shell of Ag^{II} as in the outer shell of Cu^{II}, and therefore a similar discussion is applicable. It must be assumed, however, that the $5s$ orbital in silver, as in palladium, is considerably less stable than the $4d$ orbitals (while the outer $3d$ and $4s$ orbitals in copper, as in nickel, must be assumed about equally stable). Consequently, there will be used in quadricovalent complexes of silver as in complexes of palladium $s^n d^{2-n} p^2$ square bond orbitals, with n somewhere between 1 and 0.44, the odd electron of silver being in the third $5p$ orbital.

3. THE DIFFERENT POSSIBLE ARRANGEMENTS OF FOUR spd BOND ORBITALS AND THEIR BOND-FORMING POWER

It has been shown by Kimball[10] by group theoretical considerations that it is possible to construct from s, p, and d orbitals four equivalent bond orbitals in either a tetragonal plane, a tetragonal pyramidal, a regular tetrahedral, or an irregular (trigonal axis deformed) tetrahedral arrangement, and no other. The geometrical arrangement of the strongest possible equivalent spd orbitals can thus be found by determining the angular dependence of orbitals in only these four arrangements and by determining which of the four arrangements is the best.

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[10] G. Kimball, J. Chem. Phys. **8**, 188 (1940). See also R. Hultgren, Phys. Rev. **40**, 891 (1932).

a. Tetragonal Plane Bond Orbital Arrangement

The angular parts of the s, p, and d wave functions are:[1]

$$s = 1,$$
$$p_x = \sqrt{3} \sin\vartheta \cos\varphi,$$
$$p_y = \sqrt{3} \sin\vartheta \sin\varphi,$$
$$p_z = \sqrt{3} \cos\vartheta,$$
$$d_{xy} = ((15)^{\frac{1}{2}}/2) \sin^2\vartheta \cos2\varphi, \quad (1)$$
$$d_{x+y} = ((15)^{\frac{1}{2}}/2) \sin^2\vartheta \sin2\varphi,$$
$$d_z = ((5)^{\frac{1}{2}}/2)(3 \cos^2\vartheta - 1),$$
$$d_{x+z} = (15)^{\frac{1}{2}} \sin\vartheta \cos\vartheta \cos\varphi,$$
$$d_{y+z} = (15)^{\frac{1}{2}} \sin\vartheta \cos\vartheta \sin\varphi,$$

ϑ and φ being the angles used in spherical polar coordinates.

The bond direction of a first square bond orbital will be chosen as the x direction. It is easily seen that inclusion of p_y, p_z, d_{x+y}, or d_{x+z} orbitals would cause the bond direction to be different from the x direction, so they are ignored. It can also be shown that d_{y+z} does not increase the strength of a square orbital in the x direction but decreases it, so it is ignored, too, the function thus assuming the form

$$\psi_1 = a_s s + a_p p_x + d_{dxy} d_{xy} + a_{dz} d_z. \quad (2a)$$

By rotating ψ_1 around the z axis through angles of rotation of 90°, 180°, and 270°, respectively, the other equivalent square bond orbitals are easily found to be

$$\psi_2 = a_s s + a_p p_y - a_{dxy} d_{xy} + a_{dz} d_z, \quad (2b)$$

$$\psi_3 = a_s s - a_p p_x + a_{dxy} d_{xy} + a_{dz} d_z, \quad (2c)$$

$$\psi_4 = a_s s - a_p p_y - a_{dxy} d_{xy} + a_{dz} d_z. \quad (2d)$$

The orthogonality and normalization conditions require that

$$a_s^2 + a_p^2 + a_{dxy}^2 + a_{dz}^2 = 1, \quad (3)$$

$$a_s^2 - a_p^2 + a_{dxy}^2 + a_{dz}^2 = 0, \quad (4)$$

$$a_s^2 - a_{dxy}^2 + a_{dz}^2 = 0. \quad (5)$$

We obtain from these equations the results

$$a_p^2 = \tfrac{1}{2}, \quad (6)$$

$$a_{dxy}^2 = \tfrac{1}{4}, \quad (7)$$

$$a_s^2 + a_{dz}^2 = \tfrac{1}{4}. \quad (8)$$

It is seen from (6) that there is always $\tfrac{1}{2}p$ orbital involved in a square bond orbital and thus exactly two p orbitals in each square arrangement. Furthermore, it follows from (7) that the d_{xy} orbital is used completely in each square arrangement.

We obtain, by introducing (6), (7), and (8) into (2a),

$$\psi_1 = a_s s + (1/\sqrt{2})p_x + \tfrac{1}{2}d_{xy} - (\tfrac{1}{4} - a_s^2)^{\frac{1}{2}}d_z, \quad (9)$$

Similar expressions are obtained from (2b), (2c), and (2d).

The strength S_n is easily found from (9) and (1):

$$S_n = a_s + \sqrt{3}/\sqrt{2} + ((15)^{\frac{1}{2}}/4) + ((5)^{\frac{1}{2}}/2)(\tfrac{1}{4} - a_s^2)^{\frac{1}{2}}. \quad (10)$$

The quantity S_n, as given by Eq. (10), is plotted in Fig. 1 against the amount

$$n = 4a_s^2 \quad (10a)$$

of involved s orbital.

The value of a_s corresponding to the maximum strength is found, by maximization of (10), to be $\tfrac{1}{3}$, the corresponding strength being $S = 2.943$. The angular wave functions of these strongest square bond orbitals are thus found to be

$$\psi_1 = \tfrac{1}{3}s + (1/\sqrt{2})p_x + \tfrac{1}{2}d_{xy} - ((5)^{\frac{1}{2}}/6)d_z, \quad (11a)$$

$$\psi_2 = \tfrac{1}{3}s + (1/\sqrt{2})p_y - \tfrac{1}{2}d_{xy} - ((5)^{\frac{1}{2}}/6)d_z, \quad (11b)$$

$$\psi_3 = \tfrac{1}{3}s - (1/\sqrt{2})p_x + \tfrac{1}{2}d_{xy} - ((5)^{\frac{1}{2}}/6)d_z, \quad (11c)$$

$$\psi_4 = \tfrac{1}{3}s - (1/\sqrt{2})p_y - \tfrac{1}{2}d_{xy} - ((5)^{\frac{1}{2}}/6)d_z. \quad (11d)$$

This strongest arrangement of square bond orbitals is thus composed of $4/9 s$, $14/9 d$, and two p orbitals.

It is of interest to determine the nature of the five remaining orbitals, which are orthogonal to the square bond orbitals and are not involved in bonds. There are, of course, the four orbitals p_z, d_{x+y}, d_{x+z}, and d_{y+z} that are not used in hybridization. The fifth is the orbital

$$\psi_5 = (1 - 4a_s^2)^{\frac{1}{2}}s + 2a_s d_z, \quad (12)$$

which is formed from the parts of s and d_z orbitals that are not needed in bond orbital formation. In the case of the strongest square bond orbitals (11a), (11b), (11c), (11d), ψ_5 is given by

$$\psi_5 = ((5)^{\frac{1}{2}}/3)s + \tfrac{2}{3}d_z = (5)^{\frac{1}{2}} \cos^2\vartheta, \quad (13)$$

which gives a strength of $(5)^{\frac{1}{2}}$, that is, just the strength of the best single d orbital. The possibility of using this orbital for a weak bond along the z axis is not excluded.

b. Regular Tetrahedral Bond Orbitals

We shall now look for spd hybrid orbitals for bonds directed from the central atom to the four corners of a regular tetrahedron. The bond direction of a first hybrid orbital will be chosen as the z direction. As we restrict ourselves for reasons of simplicity to cylindrical orbitals, the orbitals p_x, p_y, d_{xy}, d_{x+y}, d_{x+z}, and d_{y+z} are ignored, and the function assumes the form

$$\psi_1 = a_s s + a_p p_z + a_d d_z. \tag{14a}$$

The other three equivalent tetrahedral bond functions ψ_2, ψ_3, and ψ_4 are easily found by rotating ψ_1 first around the y axis through an angle of 109°28' (tetrahedral angle) and then around the z axis through angles 0°, 120°, and 240°, respectively.

$$\psi_2 = a_s s - \tfrac{1}{3} a_p p_z + (2\sqrt{2}/3) a_p p_x - \tfrac{1}{3} a_d d_z \\ + (4/3\sqrt{3}) a_d d_{xy} - (2\sqrt{2}/3\sqrt{3}) a_d d_{x+z}, \tag{14b}$$

$$\psi_3 = a_s s - \tfrac{1}{3} a_p p_z - (\sqrt{2}/3) a_p p_x - (\sqrt{2}/\sqrt{3}) a_p p_y \\ - \tfrac{1}{3} a_d d_z - (2/3\sqrt{3}) a_d d_{xy} + (\sqrt{2}/3\sqrt{3}) a_d d_{x+z} \\ + (\sqrt{2}/3) a_d d_{y+z} + \tfrac{2}{3} a_d d_{x+y}, \tag{14c}$$

$$\psi_4 = a_s s - \tfrac{1}{3} a_p p_z - (\sqrt{2}/3) a_p p_x + (\sqrt{2}/\sqrt{3}) a_p p_y \\ - \tfrac{1}{3} a_d d_z - (2/3\sqrt{3}) a_d d_{xy} + (\sqrt{2}/3\sqrt{3}) a_d d_{x+z} \\ - (\sqrt{2}/3) a_d d_{y+z} - \tfrac{2}{3} a_d d_{x+y}. \tag{14d}$$

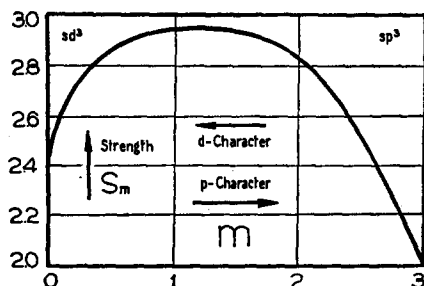We shall require that these functions be normalized to 4π and be mutually orthogonal. These

FIG. 2. Regular tetrahedral bond orbitals. Plot of the strength, S_m, against the amount, m, of p orbitals involved. As there is exactly one s orbital involved in each tetrahedral arrangement, the amount of d orbitals is $3-m$, the arrangement thus being $sp^m d^{3-m}$.

conditions lead to the relations

$$a_s^2 + a_p^2 + a_d^2 = 1, \tag{15}$$

$$a_s^2 - \tfrac{1}{3} a_p^2 - \tfrac{1}{3} a_d^2 = 0. \tag{16}$$

We obtain from these equations the result

$$a_s^2 = \tfrac{1}{4}, \tag{17}$$

$$a_p^2 + a_d^2 = \tfrac{3}{4}. \tag{18}$$

It can be seen from (17) that there is always $\tfrac{1}{4}s$ orbital involved in a tetrahedral orbital and thus exactly one s orbital in each tetrahedral arrangement.

We obtain by introducing (17) and (18) into (14a) the expression

$$\psi_1 = \tfrac{1}{2}s + a_p p_z + (\tfrac{3}{4} - a_p^2)^{\frac{1}{2}} d_z. \tag{19}$$

Similar expressions for ψ_2, ψ_3, ψ_4 are obtained from (14b), (14c), and (14d). The strength of these orbitals,

$$S_m = \tfrac{1}{2} + \sqrt{3} a_p + (5)^{\frac{1}{2}} (\tfrac{3}{4} - a_p^2)^{\frac{1}{2}}, \tag{20}$$

is shown in Fig. 2 as a function of the number $m = 4a_p^2$ of involved p orbitals, i.e., of the p character of the arrangement. The maximum strength $S_m = 2.950$ is obtained with $a_p = 3/4\sqrt{2}$, corresponding to $sd^{15/8}p^{9/8}$ orbitals. Of these orbitals we write, for reason of brevity only ψ_1, which is

$$\psi_1 = \tfrac{1}{2}s + (3/4\sqrt{2}) p_z + \tfrac{1}{4}(15/2)^{\frac{1}{2}} d_z. \tag{21}$$

The five non-bonding orbitals, which are orthogonal to the tetrahedral orbitals given by (14a), (14b), (14c), (14d), (17), and (18), may be given by the following expressions:

$$\psi_5 = (\tfrac{2}{3})^{\frac{1}{2}} d_{y+z} - (1/\sqrt{3}) d_{x+y}, \tag{22a}$$

$$\psi_6 = (\tfrac{2}{3})^{\frac{1}{2}} d_{x+z} + (1/\sqrt{3}) d_{xy}, \tag{22b}$$

$$\psi_7 = (2/3\sqrt{3})[(\tfrac{3}{4} - a_p^2)^{\frac{1}{2}}(-p_x + 2p_y - 2p_z) \\ + a_p (2d_z + 2\{(\tfrac{2}{3})^{\frac{1}{2}} d_{x+y} + (1/\sqrt{3}) d_{y+z}\} \\ - \{(\tfrac{2}{3})^{\frac{1}{2}} d_{xy} - (1/\sqrt{3}) d_{x+z}\})], \tag{22c}$$

$$\psi_8 = (2/3\sqrt{3})[(\tfrac{3}{4} - a_p^2)^{\frac{1}{2}}(2p_x - p_y - 2p_z) \\ + a_p (2d_z - \{(\tfrac{2}{3})^{\frac{1}{2}} d_{x+y} + (1/\sqrt{3}) d_{y+z}\} \\ + 2\{(\tfrac{2}{3})^{\frac{1}{2}} d_{xy} - (1/\sqrt{3}) d_{x+z}\})], \tag{22d}$$

$$\psi_9 = (2/3\sqrt{3})[(\tfrac{3}{4} - a_p^2)^{\frac{1}{2}}(2p_x + 2p_y + p_z) \\ + a_p (-d_z + 2\{(\tfrac{2}{3})^{\frac{1}{2}} d_{x+y} + (1/\sqrt{3}) d_{y+z}\} \\ + 2\{(\tfrac{2}{3})^{\frac{1}{2}} d_{xy} - (1/\sqrt{3}) d_{x+z}\})]. \tag{22e}$$

It is seen that only two of these orbitals are pure d orbitals. Furthermore, using the theorem

that the p content of any orbital is given by the sum of the squares of the coefficients of p_x, p_y, and p_z, it follows from (22c), (22d), and (22e) that each of the three dp non-bonding orbitals is composed of $(1 - (4/3)a_p{}^2)p$ orbitals and $(4/3)a_p{}^2d$ orbitals. In the case of the strongest tetrahedral orbitals $(a_p = 3/4\sqrt{2})$ each of these three orthogonal dp non-bond orbitals becomes $5/8p$ and $3/8d$ in character.

c. Comparison of Suitability of the Different Possible Bond Orbital Arrangements

In Sections 2a and 2b we were looking for arrangements of four spd bond orbitals containing exactly two p functions and being at the same time orthogonal to four pure $s-d$ orbitals. Both of these conditions are fulfilled by square bond orbital arrangements, as found in Section 3a.

These conditions, however, cannot be fulfilled simultaneously by tetrahedral orbitals (Section 3b). We can in that case fulfill the first condition by choosing $m = 4a_p{}^2 = 2$, corresponding to a sp^2d tetrahedral bond orbital arrangement. Then we see, however, from Section 3b that there are two d and three $d^{\frac{3}{3}}p^{\frac{3}{3}}$ orbitals orthogonal to the tetrahedral bond orbitals thus obtained (and not four orbitals without p character), the second condition, therefore, being unsatisfied.

A consideration, the details of which will not be given here, of irregular (trigonal axis deformed) tetrahedral and tetragonal pyramidal bond orbital functions leads to the same result as in the case of a regular tetrahedral arrangement just discussed, namely, that the two conditions mentioned above cannot be fulfilled simultaneously. Thus the square arrangement is the only arrangement of four equal bond orbitals that can be used under the conditions of Sections 2a and 2b.

In Section 2c we were looking for the four strongest spd bond orbitals that fulfill the condition of orthogonality to four $s-d$ or four pure d orbitals. On examination of the tetrahedral orbitals of Section 3b it is seen that this condition is fulfilled only in the case $m = 4a_p{}^2 = 3$, corre-

sponding to sp^3 tetrahedral orbitals of strength 2.00.

On the other hand, according to Section 3a, there can be constructed four square bond orbitals with strength 2.943 which fulfill the condition of being orthogonal to four $s-d$ orbitals, and four square bond orbitals of strength 2.694 which are orthogonal to four pure d orbitals. The strengths of these square bond orbitals are both much larger than the value 2.00 of the possible tetrahedral arrangement; this circumstance makes the tetrahedral arrangement unfavorable.

A similar consideration concerning irregular tetrahedral and tetragonal pyramidal orbitals leads to the same conclusion as in the case of regular tetrahedral orbitals. The square bond orbitals are thus seen to be the strongest four equivalent orbitals that are possible under the conditions of Section 2.

The possibility of an arrangement of non-equivalent bond orbitals that are stronger than the bond orbitals in square arrangements remains to be considered. It is not probable, however, that such an arrangement is possible.[11]

[11] This conclusion can be drawn from a treatment, the details of which are omitted, concerning the four best spd orbitals that can be arranged in such a way that the strength vectors are directed from the center toward the corners of a rhombus. Such a treatment has shown that all bond orbital arrangements having the symmetry under discussion contain exactly two p orbitals and that the four bond orbitals are orthogonal to four $s-d$ and one p orbital, just as in the limiting case of square bond orbitals. Furthermore, it can be shown that of all rhombus bond orbital arrangements of a given composition in s, p, and d, the square arrangement is the one for which the sum of the strengths (or the sum of the squares of the strengths) of the four bonding orbitals turns out to be a maximum. This circumstance makes the square arrangement favorable.