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Tetragonal Antiprism Bond Orbitals

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A set of eight equivalent bond orbitals of tetragonal antiprism symmetry is considered. The orbitals are of type $s^n p^3 d^{5-n}$. The acute angle between the fourfold axis and the maximum in a bond function varies from $66^\circ 49'$ to $44^\circ 33'$ as the parameter α is varied. The strongest orbitals (with a strength equal to 2.988) arise when n equals 0.9047. These are only slightly stronger than those with n equal to one.

COVALENT molecules or ions of type AB_8 may be formed when the electronic configuration of A is suitable and the radius of A is large enough so that the repulsion between the attached groups is low. The eight groups may be arranged about the central atom in several ways.¹⁻² Hoard and Nordsieck³ observed the dodecahedral arrangement in $[\text{Mo}(\text{CN})_8]^{4-}$. Hoard² found that TaF_8^{3-} possessed the tetragonal antiprism structure. As a step toward understanding these structures, spd bond orbitals of tetragonal antiprism symmetry are considered in this note.

The angular parts of the s , p , and d wave functions, normalized to 4π , are given by the equations

$$s = 1, \quad (1)$$

$$p_x = \sqrt{3} \sin \theta \cos \varphi, \quad (2)$$

$$p_y = \sqrt{3} \sin \theta \sin \varphi, \quad (3)$$

$$p_z = \sqrt{3} \cos \theta, \quad (4)$$

$$d_z = [(5)^{1/2}/2](3 \cos^2 \theta - 1), \quad (5)$$

$$d_{xy} = [(15)^{1/2}/2] \sin^2 \theta \cos 2\varphi, \quad (6)$$

$$d_{x+y} = [(15)^{1/2}/2] \sin^2 \theta \sin 2\varphi, \quad (7)$$

$$d_{x+z} = (15)^{1/2} \sin \theta \cos \theta \cos \varphi, \quad (8)$$

$$d_{y+z} = (15)^{1/2} \sin \theta \cos \theta \sin \varphi, \quad (9)$$

where θ and φ are the angles used in polar coordinates. Differences in the radial parts of the wave functions are

TABLE I. Results of calculations on tetragonal antiprism orbitals with $0 \leq \alpha \leq \pi/2$.

n^a	S , Strength of an orbital	θ_1 , Angle between axis and maximum in ψ_1
1.0000	2.979	$57^\circ 35'$
0.9047	2.988	$60^\circ 54'$
0.7000	2.980	$63^\circ 10'$
0.5000	2.961	$64^\circ 33'$
0.3000	2.928	$65^\circ 36'$
0.1000	2.869	$66^\circ 27'$
0.0000	2.768	$66^\circ 49'$

^a The orbitals are of type $s^n p^3 d^{5-n}$. Note that $n = \cos^2 \alpha$.

¹ G. Kimball, J. Chem. Phys. **8**, 188 (1940).

² Marchi, Ferneli, and McReynolds, J. Am. Chem. Soc. **65**, 329 (1943).

³ J. L. Hoard and H. H. Nordsieck, J. Am. Chem. Soc. **61**, 2853 (1939).

neglected and these angular parts are hybridized⁴⁻⁶ to give the desired structure.

Thus set up the following functions:

$$\psi_1 = \{[1/(8)^{1/2}] \cos \alpha\} s + [1/(8)^{1/2}] p_z + (1/2) p_x - \{[1/(8)^{1/2}] \sin \alpha\} d_z + (1/2) d_{xy} + (1/2) d_{x+z}, \quad (10)$$

$$\psi_2 = \{[1/(8)^{1/2}] \cos \alpha\} s + [1/(8)^{1/2}] p_z + (1/2) p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z - (1/2) d_{xy} + (1/2) d_{y+z}, \quad (11)$$

$$\psi_3 = \{[1/(8)^{1/2}] \cos \alpha\} s + [1/(8)^{1/2}] p_z - (1/2) p_x - \{[1/(8)^{1/2}] \sin \alpha\} d_z + (1/2) d_{xy} - (1/2) d_{x+z}, \quad (12)$$

$$\psi_4 = \{[1/(8)^{1/2}] \cos \alpha\} s + [1/(8)^{1/2}] p_z - (1/2) p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z - (1/2) d_{xy} - (1/2) d_{y+z}, \quad (13)$$

$$\psi_5 = \{[1/(8)^{1/2}] \cos \alpha\} s - [1/(8)^{1/2}] p_z + [1/(8)^{1/2}] p_x + [1/(8)^{1/2}] p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z + (1/2) d_{x+y} - [1/(8)^{1/2}] d_{x+z} - [1/(8)^{1/2}] d_{y+z}, \quad (14)$$

$$\psi_6 = \{[1/(8)^{1/2}] \cos \alpha\} s - [1/(8)^{1/2}] p_z - [1/(8)^{1/2}] p_x + [1/(8)^{1/2}] p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z - (1/2) d_{x+y} + [1/(8)^{1/2}] d_{x+z} - [1/(8)^{1/2}] d_{y+z}, \quad (15)$$

$$\psi_7 = \{[1/(8)^{1/2}] \cos \alpha\} s - [1/(8)^{1/2}] p_z - [1/(8)^{1/2}] p_x - [1/(8)^{1/2}] p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z + (1/2) d_{x+y} + [1/(8)^{1/2}] d_{x+z} + [1/(8)^{1/2}] d_{y+z}, \quad (16)$$

$$\psi_8 = \{[1/(8)^{1/2}] \cos \alpha\} s - [1/(8)^{1/2}] p_z + [1/(8)^{1/2}] p_x - [1/(8)^{1/2}] p_y - \{[1/(8)^{1/2}] \sin \alpha\} d_z - (1/2) d_{x+y} - [1/(8)^{1/2}] d_{x+z} + [1/(8)^{1/2}] d_{y+z}. \quad (17)$$

These functions represent eight equivalent orthogonal bond orbitals of type $s^n p^3 d^{5-n}$ where

$$n = \cos^2 \alpha. \quad (18)$$

TABLE II. Results of calculations on tetragonal antiprism orbitals with $0 \geq \alpha \geq -\pi/2$.

n	S , Strength of an orbital	θ_1 , Angle between axis and maximum in ψ_1
1.0000	2.979	$57^\circ 35'$
0.9000	2.955	$53^\circ 46'$
0.7000	2.927	$50^\circ 45'$
0.5000	2.897	$48^\circ 36'$
0.3000	2.859	$46^\circ 49'$
0.1000	2.797	$45^\circ 16'$
0.0000	2.696	$44^\circ 33'$

⁴ See L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

⁵ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

⁶ R. Hultgren, Phys. Rev. **40**, 891 (1932).

These orbitals are of tetragonal antiprism symmetry D_{4d} . The Z axis coincides with the fourfold axis.

A function orthogonal to ψ_1, \dots, ψ_8 is given by

$$\psi_9 = (\sin\alpha)s + (\cos\alpha)d_z. \quad (19)$$

The functions were used in constructing Tables I and II. In Table I, S and θ_1 were obtained with $0 \leq \alpha \leq \pi/2$. In Table II, S and θ_1 were obtained with $0 \geq \alpha \geq -\pi/2$. Here S is the maximum value of ψ_1 and is called the strength of an orbital; θ_1 is the angle between the axis and the maximum in ψ_1 and is approximately the angle between the axis and bond one.

It is evident that the orbitals described in Table I will be preferred since they are stronger than the corresponding ones in Table II. The strongest tetragonal antiprism orbitals may be formed when n equals 0.9047. The maximum strength, 2.988, is only slightly less than the maximum strength⁶ of an spd orbital. When the s

and d orbitals are of almost equal stability, n will tend to equal 0.9047 if the tetragonal antiprism structure is assumed.

Kimball¹ reasoned that the stable bond arrangement when n equaled one was the dodecahedral arrangement since $[\text{Mo}(\text{CN})_8]^{-4}$ has this structure. However, one would conclude from the present calculations that the tetragonal antiprism structure is one of the stable structures when n equals one.

Because of the repulsion between the attached groups in the tetragonal antiprism structure, the acute angle between the axis and a bond will tend to be different from θ_1 for all but one value of n and the effective strength of the orbitals will be reduced somewhat. If the repulsion tends to stabilize the regular tetragonal antiprism structure, this acute angle would tend to be between θ_1 and $59^\circ 16'$. (Here a regular tetragonal antiprism is defined as the square antiprism with sixteen equal edges.)

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Compressibilities, Force Constants, and Interatomic Distances of the Elements in the Solid State

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Available data for the compressibilities of crystalline elements are used to calculate the force constants for the assumed Hooke's law interactions between adjacent atoms. On comparison of these constants and the equilibrium interatomic distances it is found that for many substances there holds the relation discovered by Badger for diatomic gas molecules: a linear relation between the reciprocal of the cube root of the force constant and the interatomic distance, for elements of a given row in the periodic table. Deviations from this relation are in the direction of increased compressibility. They are explained as resulting from changes in bond type (that is, in electronic structure) that permit the crystal to adjust itself to the increased pressure.

INTRODUCTION

THE compressibilities of elements and compounds in the solid state¹ represent a considerable body of information which may be interpreted in terms of molecular constants. An attempt is made here to do this for substances which have simple structures, mainly those with cubic symmetry. Our considerations have been based on the concept of the existence of covalent bonds between nearest neighbors in the lattice (resonating covalent bonds in the metals). The compressibility is then used to evaluate the force constant for a Hooke's law force acting along the bonds. A relationship similar to Badger's rule² for molecules in the gaseous state has been found to obtain between these force constants and the interatomic distances.

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† Contribution No. 1380.

¹ See P. W. Bridgman, *Rev. Mod. Phys.* **18**, 1 (1946).

² R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934); **3**, 710 (1935).

There exists one difficulty with the attempt to use central forces to explain the elastic properties of crystalline matter, especially in the case of metals. Central forces imply certain relations among the various elastic constants of a crystal, the Cauchy relations, which are poorly satisfied for metals.³ Non-central forces should, therefore, be introduced in addition to the central forces assumed above. In the usual electron theory of metals the interactions between the free electrons and the lattice of residual ion cores are of the non-central type, and the breaking down of the Cauchy relations may be thus accounted for. If all elastic constants are known for a given crystal the contributions to the energy of the crystal from the free electrons may be separated

³ It was recently pointed out by P. S. Epstein (*Phys. Rev.* **70**, 915 (1946)) that the Cauchy relations are not expected to hold for the general case of central forces involving non-nearest neighbors also. However, they should be satisfied for central forces between nearest neighbors only. Cf. also C. Zener, *Phys. Rev.* **71**, 323 (1947).