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Hexacovalent Bond Orbitals I

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A set of six equivalent orthogonal bond orbitals of type $s^np^{1+2m}d^{5-n-2m}$ are considered. The fact that these are of trigonal prism symmetry is pointed out. Calculations were made of the bond strengths and angles at various values of m with n set equal to one and at various values of n with m set equal to zero.

THE method of directed valence bonds has been employed[1-3] in discussing hexacovalent structures possessing equivalent cylindrical bonds. Two structures were found, the octahedral structure and the trigonal prism structure. However, the trigonal prism structure is observed when $1s$, $1p$, and $4d$ orbitals are readily available for bond formation. The structure discussed by Hultgren employed $17/18s$, $7/3p$, and $49/18d$ orbitals. It seems of interest to consider more general hexacovalent orbitals.

In this paper some calculations are reported on a set of orbitals which yields the trigonal prism configuration. The set is formed by spd hybridization.

Differences in the radial parts of the s, p, and d wave functions are neglected. Then the angular parts, normalized to 4π, are given by the equations

$$s=1, \tag{1}$$

$$p_x=\sqrt{3}\sin\theta\cos\varphi, \tag{2}$$

$$p_y=\sqrt{3}\sin\theta\sin\varphi, \tag{3}$$

$$p_z=\sqrt{3}\cos\theta, \tag{4}$$

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

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

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

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

and

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

where θ and φ are the angles used in polar coordinates. The following functions are formed:

$$\psi_1=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s+[1/(6)^{\frac{1}{2}}]p_z+[(1/\sqrt{3})\cos\beta]p_x+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z+[(1/\sqrt{3})\sin\beta]d_{xy}+(1/\sqrt{3})d_{x+z}, \tag{10}$$

$$\psi_2=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s+[1/(6)^{\frac{1}{2}}]p_z-[(1/2\sqrt{3})\cos\beta]p_x+[(1/2)\cos\beta]p_y+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z-[(1/2\sqrt{3})\sin\beta]d_{xy}-[(1/2)\sin\beta]d_{x+y}-(1/2\sqrt{3})d_{x+z}+(1/2)d_{y+z}, \tag{11}$$

$$\psi_3=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s+[1/(6)^{\frac{1}{2}}]p_z-[(1/2\sqrt{3})\cos\beta]p_x-[(1/2)\cos\beta]p_y+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z-[(1/2\sqrt{3})\sin\beta]d_{xy}+[(1/2)\sin\beta]d_{x+y}-(1/2\sqrt{3})d_{x+z}-(1/2)d_{y+z}, \tag{12}$$

$$\psi_4=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s-[1/(6)^{\frac{1}{2}}]p_z+[(1/\sqrt{3})\cos\beta]p_x+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z+[(1/\sqrt{3})\sin\beta]d_{xy}-(1/\sqrt{3})d_{x+z}, \tag{13}$$

$$\psi_5=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s-[1/(6)^{\frac{1}{2}}]p_z-[(1/2\sqrt{3})\cos\beta]p_x+[(1/2)\cos\beta]p_y+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z-[(1/2\sqrt{3})\sin\beta]d_{xy}-[(1/2)\sin\beta]d_{x+y}+(1/2\sqrt{3})d_{x+z}-(1/2)d_{y+z}, \tag{14}$$

$$\psi_6=\{[1/(6)^{\frac{1}{2}}]\cos\alpha\}s-[1/(6)^{\frac{1}{2}}]p_z-[(1/2\sqrt{3})\cos\beta]p_x-[(1/2)\cos\beta]p_y+\{[1/(6)^{\frac{1}{2}}]\sin\alpha\}d_z-[(1/2\sqrt{3})\sin\beta]d_{xy}+[(1/2)\sin\beta]d_{x+y}+(1/2\sqrt{3})d_{x+z}+(1/2)d_{y+z}. \tag{15}$$

These functions represent six equivalent orthogonal bond orbitals of type $s^np^{1+2m}d^{5-n-2m}$ where

$$n=\cos^2\alpha \tag{16}$$

and

$$m=\cos^2\beta. \tag{17}$$

the functions reduce to the functions given by Hultgren[3] for equivalent, cylindrical, regular[4] trigonal prism orbitals when $\cos\alpha=(34)^{\frac{1}{2}}/6$ and $\cos\beta=\sqrt{2}/\sqrt{3}$. Changing α and β from the values obtained from these equations makes the bonds non-cylindrical but it does not destroy the trigonal prism symmetry.

In each case the axis of the regular trigonal prism coincides with the Z axis. Let the numbering of the bonds be the same as the numbering of the ψ_i. Thus bond one is described by ψ_1. Bonds one, two, and three lead to atoms in one base of the regular trigonal prism. Bonds four, five, and six lead to the corresponding atoms in the other base.

Three orbital functions orthogonal to $\psi_1, \psi_2, \cdots\psi_6$ can be set up as follows:

$$\psi_7=(\sin\alpha)s-(\cos\alpha)d_z, \tag{18}$$

$$\psi_8=(\sin\beta)p_x-(\cos\beta)d_{xy}, \tag{19}$$

$$\psi_9=(\sin\beta)p_y+(\cos\beta)d_{x+y}. \tag{20}$$

[1] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).
[2] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).
[3] R. Hultgren, Phys. Rev. **40**, 891 (1932).
[4] A regular trigonal prism is a right prism whose bases are equilateral triangles.

TABLE I. Results of calculations on trigonal prism orbitals of type $sp^{1+2m}d^{4-2m}$.

m	S, Strength of a bond	θ_1, Angle between axis and bond 1
1.0000	2.737	47° 5′
0.9800	2.817	48° 36′
0.9000	2.898	50° 17′
0.8000	2.944	51° 23′
0.5575	2.979	52° 50′
0.3000	2.943	53° 29′
0.2000	2.904	53° 30′
0.1000	2.838	53° 18′
0.0200	2.727	52° 40′
0.0000	2.623	51° 52′

TABLE II. Results of calculations on trigonal prism orbitals of type s^npd^{5-n}.

n	S, Strength of a bond	θ_1, Angle between axis and bond 1
1.0000	2.623	51° 52′
0.9800	2.631	49° 47′
0.9600	2.634	48° 54′
0.9000	2.640	47° 7′
0.8000	2.644	45° 4′
0.7094	2.645	43° 37′
0.3000	2.620	38° 55′
0.2000	2.601	38° 1′
0.1000	2.569	37° 12′
0.0000	2.462	36° 25′

In the calculations reported in Table I n was set equal to one. A value was assigned to m. Then θ_1, the angle between the axis and bond one, was determined by finding the position of the maximum in ψ_1. The corresponding value of ψ_1 gave the strength of the bond, S. In the calculations reported in Table II m was set equal to zero. Then θ_1 and S were determined as before.

The strongest bonds when n equals one occur when m equals 0.5575. These bonds have a strength equal to 2.979. This is only slightly smaller than the value 2.982 reported by Hultgren[3] for cylindrical trigonal prism orbitals. The strongest bonds when m equals zero occur when n equals 0.7094. These bonds have a strength equal to 2.645.

It is evident that the bond angles change somewhat as the composition of the bonds is altered. Thus one may obtain some information about the composition of the bonds from the observed bond angles.

As an example consider the MoS_2 crystal. The sulfur atoms are arranged in the form of trigonal prisms[1,5] about the molybdenum atoms. If the unshared pair outside the core of a molybdenum atom is put into a d orbital, then $1s$, $1p$, and $4d$ orbitals are available for bond formation. Hence one might expect the trigonal prism structure to be assumed with the angle between bond one and the axis equal to 51° 52′. However, stronger bonds may be formed if m does not equal zero (more of the unstable p orbitals used for shared pairs) and if n does not equal one. The unshared pair may go into the orbital described by ψ_7. The actual composition used may be estimated following the method of Kuhn.[6] That such bonds are formed is indicated by the fact that the observed[1,5] angle between bond one and the axis is 49°.

[5] R. G. Dickinson and L. Pauling, J. Am. Chem. Soc. **45**, 1466 (1923).
[6] H. Kuhn, J. Chem. Phys. **16**, 727 (1948).