

Textbook Errors, 81

The Five Equivalent d Orbitals

Several textbooks¹ assert that there is no way of choosing the five d orbitals so that they have the same shape but differ only in their orientation; and, so far as the writer is aware, no textbook author has written down such a set of d orbitals. Yet, as early as 1940, George E. Kimball, in his classic memoir on the application of group theory to directed valence (1), pointed out that five equivalent d orbitals could be directed along the slant edges of a pentagonal pyramid. If for no other reason than to call attention to Kimball's result, it seems worth while to set down here the five orbitals.

Group-Theoretic Proof of Existence

The reader who is unfamiliar with group theory may skip at once to the following section, or he may refer to a monograph such as Cotton's (2).

The first step in the proof is to evaluate the set of characters for the representation based upon a pentagonal pyramid, most simply by counting the number of orbitals, directed along the slant edges of a pentagonal pyramid, which remain unshifted by each of the four possible symmetry operations. The identity operation, E , leaves all 5 orbitals unshifted. The rotation by one-fifth a turn, C_5 , leaves none unshifted. So does the rotation by two-fifths a turn, C_5^2 . The operation of reflection through a vertical plane (i.e., a plane passing through the axis and one orbital), σ_v , leaves one orbital unshifted. In summary,

$$\Gamma(\text{pentagonal pyramid}) = \begin{matrix} E, & C_5, & C_5^2, & \sigma_v \\ 5, & 0, & 0, & 1 \end{matrix}$$

The second step in the proof is to express this representation as a linear combination of irreducible representations.

Table I. Character Table for the Group C_{5v}

	E	$2 C_5$	$2 C_5^2$	$5 \sigma_v$
A_1	1	1	1	1
A_2	1	1	1	-1
E_1	2	$2 \cos \pi/5$	$2 \cos 2\pi/5$	0
E_2	2	$2 \cos 2\pi/5$	$2 \cos \pi/5$	0

representations for the symmetry group C_{5v} . The standard procedure is to multiply the characters just found by the corresponding characters of each irreducible representation as listed in the Character Table for C_{5v} , (Table I), to sum the resulting products after

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¹ Since the purpose of this column is to prevent the spread and the continuation of errors and not the evaluation of individual texts, the sources of errors discussed will not be cited. In order to be presented an error must occur in at least two independent recent standard books.

multiplying each by the number of such operations, and to divide the total by the order of the group, in this instance 10. The result is for A_1 , 1; for A_2 , 0; for E_1 , 1; and for E_2 , 1. In summary,

$$\Gamma(\text{pentagonal pyramid}) = A_1 + E_1 + E_2$$

The third and last step in the proof is to ascertain whether or not the set of five d orbitals provides a basis for this same representation. It does. The d_{z^2} orbital transforms like A_1 , the pair d_{xz} and d_{yz} like E_1 , and the pair $d_{x^2-y^2}$ and d_{xy} like E_2 . This completes the proof.

One further conclusion can be reached without numerical computation. Since the d orbitals are *gerade*, i.e., symmetric with respect to the center of inversion, the five equivalent orbitals must extend in both directions, along the slant edges of two pentagonal pyramids with a common vertex, as in the structure of ferrocene (Fig. 1). This is the symmetry of the *gerade* representations of the D_{5d} group, the pentagonal anti-prism.

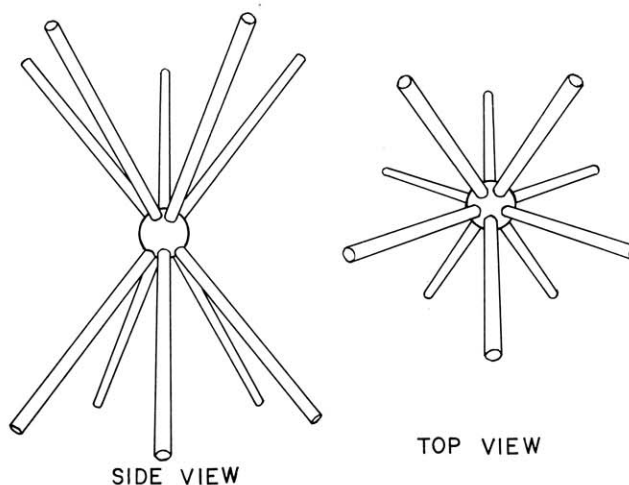


Figure 1. The directions of the five equivalent d orbitals.

The Shape of the Orbitals

Let us label the five pyramidal d orbitals by the fractions of a full turn by which they are rotated around the z axis, viz., d_0 , $d_{1/5}$, $d_{2/5}$, $d_{3/5}$, and $d_{4/5}$. Each of them has to be expressible as a linear combination of the five d orbitals in any other representation. Thus,

$$d_0 = c_1 d_{z^2} + c_2 d_{xz} + c_3 d_{yz} + c_4 d_{x^2-y^2} + c_5 d_{xy}$$

Inasmuch as the d_{z^2} orbital is unaffected by the operations of rotation or reflection, it must contribute equally to all five pyramidal orbitals; therefore, apart from sign, the coefficient c_1 is $\sqrt{1/5}$. Consider, now, the pyramidal orbital at $\phi = 0$. Reflection in a vertical

plane must leave it unchanged; d_{xz} , which is proportional to $\cos \phi$, and $d_{x^2-y^2}$, which is proportional to $\cos 2\phi$, are unchanged by that reflection; but d_{yz} , which is proportional to $\sin \phi$, and d_{xy} , which is proportional to $\sin 2\phi$, go into their negatives by that reflection; wherefore, the coefficients c_3 and c_5 must be zero. Inasmuch as the sum of squares of coefficients has to be unity, $c_2^2 + c_4^2 = 4/5$. Consider, next, the orthogonality of the several orbitals to one another. Upon forming $d_{1/5}$ by replacing ϕ by $(\phi - 2\pi/5)$ and then multiplying each coefficient of $d_{1/5}$ by the corresponding coefficient of d_0 , we obtain a sum which orthogonality requires to be zero, viz.,

$$1/5 + c_2^2 \cos 2\pi/5 - c_4^2 \cos \pi/5 = 0$$

The orthogonality of $d_{2/5}$ with d_0 gives

$$1/5 - c_2^2 \cos \pi/5 + c_4^2 \cos 2\pi/5 = 0$$

But for these simultaneously to be true requires $c_2^2 = c_4^2$. Hence, apart from sign, $c_2 = c_4 = \sqrt{2/5}$. For the moment taking all three coefficients as positive, we have

$$d_0 = \sqrt{1/5} d_{z^2} + \sqrt{2/5} d_{xz} + \sqrt{2/5} d_{x^2-y^2}$$

Once these coefficients for d_0 have been obtained, the coefficients for all the other four orbitals are uniquely determined. One need only replace d_{xz} and $d_{x^2-y^2}$ by the orbitals into which each of them is transformed upon replacing ϕ successively by $\phi - 2\pi/5$, $\phi - 4\pi/5$, $\phi - 6\pi/5$, and $\phi - 8\pi/5$. The full results, written in matrix form for the sake of compactness, are given in Table 2. Since the five pyramidal d orbitals constitute

Table 2. Coefficients Giving the Pyramidal d Orbitals

d_0	$\sqrt{\frac{1}{5}}$	$\sqrt{\frac{2}{5}}$	0	$\sqrt{\frac{2}{5}}$	0	d_{z^2}
$d_{1/5}$	$\sqrt{\frac{1}{5}}$	$\sqrt{\frac{2}{5}} \cos \frac{2\pi}{5}$	$\sqrt{\frac{2}{5}} \sin \frac{2\pi}{5}$	$-\sqrt{\frac{2}{5}} \cos \frac{\pi}{5}$	$\sqrt{\frac{2}{5}} \sin \frac{\pi}{5}$	d_{xz}
$d_{2/5}$	$\sqrt{\frac{1}{5}}$	$-\sqrt{\frac{2}{5}} \cos \frac{\pi}{5}$	$\sqrt{\frac{2}{5}} \sin \frac{\pi}{5}$	$\sqrt{\frac{2}{5}} \cos \frac{2\pi}{5}$	$-\sqrt{\frac{2}{5}} \sin \frac{2\pi}{5}$	d_{yz}
$d_{3/5}$	$\sqrt{\frac{1}{5}}$	$-\sqrt{\frac{2}{5}} \cos \frac{\pi}{5}$	$-\sqrt{\frac{2}{5}} \sin \frac{\pi}{5}$	$\sqrt{\frac{2}{5}} \cos \frac{2\pi}{5}$	$\sqrt{\frac{2}{5}} \sin \frac{2\pi}{5}$	$d_{x^2-y^2}$
$d_{4/5}$	$\sqrt{\frac{1}{5}}$	$\sqrt{\frac{2}{5}} \cos \frac{2\pi}{5}$	$-\sqrt{\frac{2}{5}} \sin \frac{2\pi}{5}$	$-\sqrt{\frac{2}{5}} \cos \frac{\pi}{5}$	$-\sqrt{\frac{2}{5}} \sin \frac{\pi}{5}$	d_{xy}

a complete orthogonal set, the process can be reversed to give the more familiar cubic d orbitals as linear combinations of the pyramidal. The inversion of the matrix is left as an exercise for the student.

Upon inserting the known angular functions (normalized to unity) for d_{z^2} , d_{xz} , and $d_{x^2-y^2}$, we obtain the following explicit expression for the angular dependence of the d_0 orbital:

$$d_0 = (3/8\pi)^{1/2} [(1/6)^{1/2} (3 \cos^2 \theta - 1) + \sin 2\theta \cos \phi + \sin^2 \theta \cos 2\phi]$$

Apart from rotation by successive one-fifth turns around the z axis, the other pyramidal orbitals have this same angular dependence. Each orbital has its maximum at $\theta = 41^\circ 47.65'$, i.e., tipped up from the equatorial plane at an angle of $48^\circ 12.35'$. The model from which Figure 1 was sketched was built to these specifications.

Figures 2 through 7 display the calculated "shape" of any one pyramidal d orbital, as follows: Figure 2, side

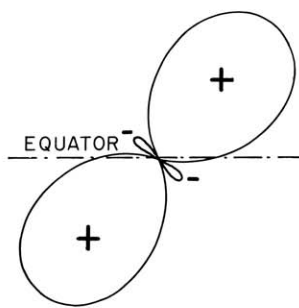


Figure 2. Angular factor of eigenfunction for a pyramidal d orbital, side view.

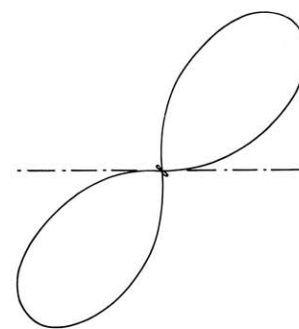


Figure 3. Square of angular factor, side view.

view of the angular factor of the eigenfunction; Figure 3, square of the same; Figure 4, side view of contour map of position probability density (at 10% intervals from its maximum value), constructed by multiplying the square of the angular factor by $r^4 e^{-r}$, the radial factor appropriate to a $3d$ orbital; Figure 5, top view

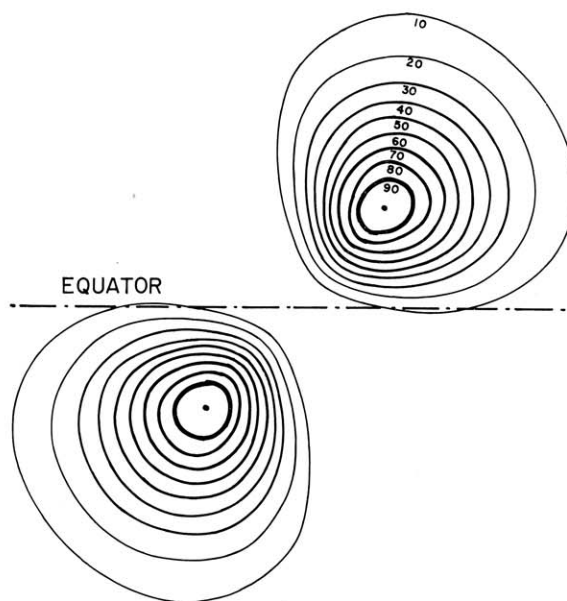


Figure 4. Position probability contours, side view.

(looking down the z axis) of the angular factor in section through the plane of its maximum; Figure 6, square of the same; and Figure 7, top view of position probability contours.

Unlike the familiar four-lobed cubic d orbital, the pyramidal d orbital has only rather inconspicuous lobes

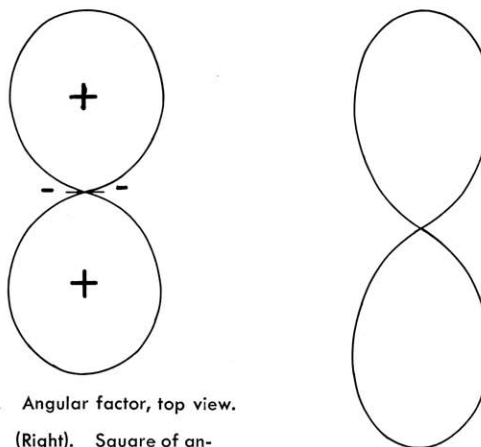


Figure 5. Angular factor, top view.

Figure 6. (Right). Square of angular factor, top view.

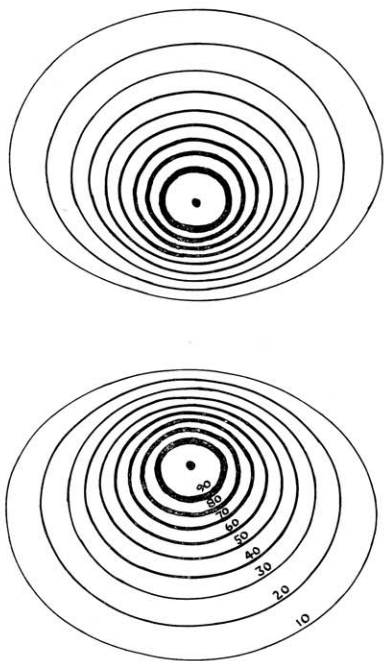


Figure 7. Position probability contours, top view.

of opposite sign. Each orbital is not quite cylindrically symmetrical about its own axis of maximum probability.

It will be recalled that provisionally we took all three coefficients in d_0 to be positive. Let us now return to that question. The signs are not settled by symmetry arguments, so that in principle each of the three could be positive or negative, giving $2^3 = 8$ sign combinations in all. However, three-fourths of these are trivial: they correspond to the principal lobe having negative rather than positive sign, or to it being directed to the second quadrant of θ rather than the first. There remain, however, two choices of sign which do lead to orbitals differing in shape. One we have discussed, which has all signs positive. The other has c_1 negative but c_2 and c_4 positive. The side view of the resulting orbital is shown in Figure 8. The principal lobe is tipped up at an angle of only $20^\circ 58.65'$ from the equatorial plane, and the lobes of opposite sign are comparatively large. Thus there exist not one, but two, sets of 5 equivalent d orbitals.

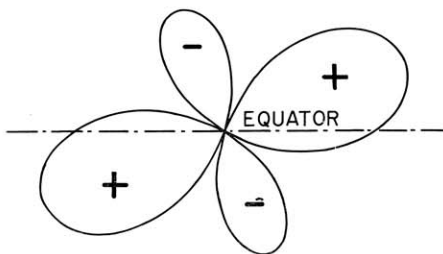


Figure 8. Angular factor of alternative pyramidal eigenfunction, side view.

Bond Formation

The geometry of the pyramidal d orbitals suggests that, to the Valence Bond approximation, equivalent d bonds could be made to cyclopentadiene in the metal cyclopentadienyls. For instance, $Tl(C_5H_5)$ could have five two-electron d bonds, and ferrocene, $Fe(C_5H_5)_2$, could have ten one-electron d bonds, the remaining

electrons occupying non-bonding s^2p^6 orbitals, giving the central metal atom an 18-electron rare gas configuration. This approximation has undoubtedly some merit. It is, however, naive on several counts. (1) There must occur mixing of d orbitals with other orbitals having the same symmetry. In ferrocene, for instance, the d_{z^2} orbital and the s orbital have the same symmetry, so that the appropriate binding orbital has to be a hybrid of the two. For $Tl(C_5H_5)$, whose bonds do not have to be possess central symmetry, there can be additional hybridization with a p_z orbital. (2) The p orbitals, even though they have the wrong symmetry to mix with the d orbitals, may form orbitals of significant stability with the ligand rings. (3) The presence of the ligands will, in general, split the degeneracy of the otherwise equivalent orbitals. In ferrocene, the metal-to-carbon bond is tipped up from the equatorial plane some 6 degrees farther than the pyramidal d orbitals, and the splitting between the highest and the lowest d molecular orbital is computed to be 3.08 to 4.63 ev. The reader who is interested in pursuing these bonding questions is referred to the considerable literature on MO calculations for metal cyclopentadienyls (3-8).

Other Pyramidal Orbitals

The same line of argument applies to orbitals of other azimuthal quantum numbers. Thus, there are three equivalent p orbitals (one set) directed along the slant edges of a trigonal pyramid; seven equivalent f orbitals (four different sets) directed along the slant edges of a heptagonal pyramid; nine equivalent g orbitals (eight different sets) directed along the slant edges of a nine-sided pyramid; and so on.

For p orbitals, this is a well known result. Taking the z axis as the axis of rotational symmetry and proceeding as above, we easily obtain

$$p_0 = \sqrt{1/3} p_z + \sqrt{2/3} p_x$$

This gives for the angular factor,

$$p_0 = (1/4\pi)^{1/2} \cos \theta + (1/2\pi)^{1/2} \sin \theta \cos \phi$$

which corresponds to a p orbital of the familiar shape, tipped up at $35^\circ 16'$ from the equatorial plane.

For f orbitals, the pyramidal orbital is given by

$$f_0 = \sqrt{1/7} f_z^3 + \sqrt{2/7} f_{\cos \phi} + \sqrt{2/7} f_{\cos 2\phi} + \sqrt{2/7} f_{\cos 3\phi}$$

which gives, for its explicit angular dependence,

$$f_0 = (1/16\pi)^{1/2} [(5 \cos^2 \theta - 3 \cos \theta) + 3^{1/2} \sin \theta (5 \cos^2 \theta - 1) \cos \phi + 30^{1/2} \sin^2 \theta \cos \theta \cos 2\phi + 5^{1/2} \sin^3 \theta \cos 3\phi]$$

As written, this pyramidal f orbital has all its coefficients positive; but there are three other combinations, with a principal lobe of positive sign in the first quadrant. They have signs $-+++$, $--++$, and $+++-$, respectively. The orbital with all-plus coefficients has two strong oppositely-directed lobes, with rather small intermediate lobes. The other three sets have successively larger intermediate lobes.

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