

DIRECTED VALENCES

COMMUNICATION 1. DIRECTIONS AND MAXIMUM VALUES OF HYBRID FUNCTIONS FOR COORDINATION NUMBERS 2, 3, AND 4

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In 1940 Kimball developed a method [1] for establishing the set of atomic functions that give hybrid orbits corresponding to a definite bond configuration. This method, which made it possible to establish the set of atomic functions corresponding to a given bond configuration, did not solve the reverse problem of predicting the arrangement of the bonds from a known electronic configuration. Actually, in a number of cases, various arrangements of hybrid orbits are possible with the same set of s-, p-, d-, and f-electrons. We should mention that ambiguity arises only when one of the possible groups is not a subgroup of the other. If, however, a given set of functions may result in two symmetries, of which one is a subgroup of the other, for example, C_{3v} and D_{3h} , one may readily show that the orbits will have the symmetry C_{3v} and also D_{3h} , and a greater degree of symmetry will be achieved.

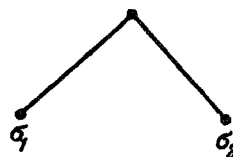
A knowledge of the set of functions corresponding to a given configuration gives no indication of the stability of the bonds formed and does not make it possible to compare the advantages of various configurations and various bonds within a configuration in the case of nonequivalent hybrid orbits which are not interconvertible by symmetry rearrangements. In those cases when various valence angles are compatible with a given symmetry, group theory does not solve the problem of the sizes of the angles. In this work we attempted to answer these problems and the coordination numbers 2, 3, and 4 are examined in Part I and numbers 5 to 9 in Part II. The fundamental premise is that all these problems may be solved on the basis of the criterion that bonds form in the direction of the maximum concentration of the electron cloud. For this purpose we determined the analytic expressions, the directions of maximum concentration and the maximum values of the hybrid orbits. With this data it is possible to solve the problem of valence angles and relative "strength" of individual bonds when nonequivalent bonds are presented and also to undertake the problem selecting the configuration. One may consider that if a given set of s-, p-, d-, and f-electrons corresponds to several different symmetries, then there will be a configuration with a maximum concentration of bonding orbits in the direction of the bonds and most favorable angles.

The analytical expressions of hybrid orbits were found in the following way. Each system of valence orbits gives a basis for a representation of the group. By rearrangement, a series is developed into subgroups and each subgroup is a basis for an unreduced representation of the group. The same also applies to the series of atomic orbits. A comparison of unreduced representations of valence orbit systems with the representations of atomic orbits makes it possible to establish the combination of atomic functions which corresponds to the system of valence orbits of the required symmetry. By comparing the atomic and valence orbits belonging to the same unreduced representation and taking into account the conditions of normalization and orthogonality, we drew up equations for the relation between the valence and hybrid orbits. By solving these relations with respect to the hybrid orbits σ_i , we can find their analytical expressions through a linear combination of the atomic orbits. The direction of maximum concentration and the maximum values of hybrid orbits are found by solving the following equations:

$$\frac{\partial \sigma_i}{\partial \vartheta_i} = 0 \text{ and } \frac{\partial \sigma_i}{\partial \varphi_i} = 0. \quad (1)$$

Coordination number 2
 C_{2v} symmetry (Fig. 1)

$$\sigma_{1,2} = \frac{1}{\sqrt{2}}(a \pm b)$$



Hybridization	$\angle \sigma_1 \sigma_2$	M	Δ
sd_{xz}	90°	2,076	1,216
$sf_z(x^2 - y^2)$	$70^\circ 32'$	2,102	1,232
$p_x p_z$	90°	1,732	0
$p_x d_{xz}$	$74^\circ 20'$	2,295	0,922
$p_x f_z(x^2 - y^2)$	$82^\circ 10'$	2,277	0,850
$d_{z^2} d_{xz}$	$130^\circ 53'$	2,209	0,246
$d_{x^2-y^2} d_{xz}$	$63^\circ 26'$	2,215	0,558
$d_{x^2-y^2} f_z(x^2 - y^2)$	$55^\circ 24'$	2,395	0,882
$f_{xz^3} p_z$	$122^\circ 58'$	2,641	1,313
$f_{xz^3} d_{xz}$	$98^\circ 08'$	2,752	1,337
$f_{xz^3} f_z^3$	$145^\circ 46'$	2,607	0,337
$f_{xz^3} f_z(x^2 - y^2)$	101°	2,572	0,941
$f_x(x^2 - y^2) d_{xz}$	$54^\circ 10'$	2,153	0,279
$f_x(x^2 - y^2) f_z(x^2 - y^2)$	$49^\circ 50'$	2,359	0,515

$D_{\infty h}$ symmetry (Fig. 2)

$$\sigma_{1,2} = \frac{1}{\sqrt{2}}(a \pm b)$$



Hybridization	$\angle \sigma_1 \sigma_2$	M	Δ
sp_z	180°	1,932	1,132
sf_z^3	180°	2,578	1,510
d	180°	2,806	1,644
$d_{z^2} f_z^3$	180°	3,453	2,024

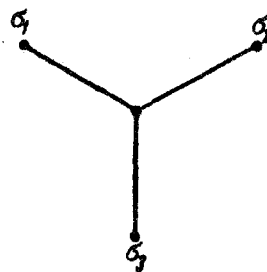
We use Δ to designate the difference between the sum of the maximum values of the hybrid functions (M) and the sum of the maximum values of separate single-electron atomic functions which participate in the hybridization. The value Δ must to some extent serve as a criterion of the energy advantage of one or other configuration. Below we give the analytical expressions, angles between the directions of maximum concentrations, the maximum values of the hybrid orbits and the values of Δ^* for a series of possible hybridizations corresponding to various symmetries. We supplemented Kimball's data in previous work where we examined the configurations of bonds with C_{2v} symmetry at a coordination number (c.n.) of 4 ($TeCl_4$ configuration), C_{3v} at c.n. 6 (deformed octahedron), D_{5h} at c.n. 7 (five-faced bipyramid), D_{3h} at c.n. 8 (three-faced prism with two extra atoms above the centers of the triangular faces) and c.n. 9 (three-faced prism with three extra atoms above the centers of the rectangular faces) [2-5].

* In some cases Δ is negative and this indicates the disadvantage of hybridization. These data are not included in the tables.

Coordination Number 3
 D_{3h} symmetry (Fig. 3)

$$\sigma_1 = \frac{1}{\sqrt{3}} a + \frac{2}{\sqrt{6}} b$$

$$\sigma_{2,3} = \frac{1}{\sqrt{3}} a - \frac{1}{\sqrt{6}} b \pm \frac{1}{\sqrt{2}} c$$

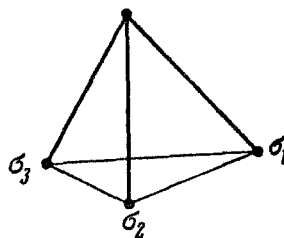


Hybridization	Angles between the directions of the maximum values of hybrid functions	M	Δ
$sp_x p_y$	120°	1,991	1,509
$sd_{xy} d_{x^2-y^2}$	120°	2,159	1,605
$sf_{xz^2} f_{yz^2}$	120°	1,900	0,237
$d_z d_{xy} d_{x^2-y^2}$	120°	2,226	0,570
$d_z p_x p_y$	120°	2,059	0,477
$f_{x(x^2-y^2)} p_x p_y$	120°	2,622	2,311
$f_{x(x^2-y^2)} d_{xy} d_{x^2-y^2}$	120°	2,653	1,996

C_{3v} symmetry (Fig. 4)

$$\sigma_1 = \frac{1}{\sqrt{3}} a + \frac{2}{\sqrt{6}} b$$

$$\sigma_{2,3} = \frac{1}{\sqrt{3}} a - \frac{1}{\sqrt{6}} b \pm \frac{1}{\sqrt{2}} c$$

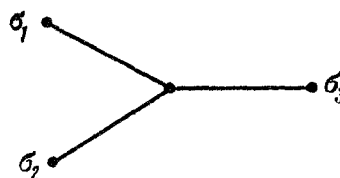


Hybridization	$\angle \sigma_1 \sigma_2$	M	Δ
$sd_{xz} d_{yz}$	75°30'	2,158	1,602
$sf_{xz^2} f_{yz^2}$	52°50'	2,399	1,734
$sf_{z(x^2-y^2)} f_{xyz}$	90°	2,187	1,617
$p_z p_x p_y$	90°	1,732	0
$d_z d_{xz} d_{yz}$	50°04'	2,177	0,423
$p_z d_{xz} d_{yz}$	66°26'	2,324	1,368
$p_z f_{xz^2} f_{yz^2}$	49°38'	2,686	1,864
$p_z f_{z(x^2-y^2)} f_{xyz}$	83°06'	2,221	0,981
$d_z f_{xz^2} f_{yz^2}$	43°30'	2,684	1,354
$f_{x(x^2-y^2)} d_{xz} d_{yz}$	94°22'	2,157	0,508
$f_z f_{xz^2} f_{yz^2}$	35°	2,562	0,578
$f_z f_{z(x^2-y^2)} f_{xyz}$	112°24'	2,726	1,598
$f_{x(x^2-y^2)} f_{z(x^2-y^2)} f_{xyz}$	100°16'	2,363	1,054

C_{2v} symmetry (Fig. 5)

$$\sigma_3 = \frac{1}{\sqrt{3}} a + \frac{2}{\sqrt{6}} b$$

$$\sigma_{1,2} = \frac{1}{\sqrt{3}} a - \frac{1}{\sqrt{6}} b \pm \frac{1}{\sqrt{2}} c$$



Hybridization	Angles between the directions of the maximum values of hybrid functions		M		Δ
	σ_1 $\sigma_1 \sigma_2$	$\sigma_1 \sigma_2$	σ_1	σ_1, σ_2	
$sf_{xz^2}f_y(x^2-y^2)$	151°23'	57°14'	1,900	2,633	1,844
$sf_{x(x^2-y^2)}f_{yz^2}$	116°12'	127°36'	2,285	2,442	1,847
$sf_{x(x^2-y^2)}f_y(x^2-y^2)$	160°	40°	2,285	2,285	1,673
sp_xd_{xy}	139°50'	80°20'	1,991	2,467	2,257
$sp_yd_{z^2}$	90°	180°	2,403	2,258	1,951
$sp_yd_{x^2-y^2}$	90°	180°	2,158	2,592	2,674
$sp_xf_{yz^2}$	121°41'	116°38'	1,991	1,924	0,876
$sp_xf_y(x^2-y^2)$	151°27'	57°06'	1,991	2,671	2,510
$sp_yf_{xz^2}$	118°22'	123°16'	1,900	1,969	0,875
$sp_yf_x(x^2-y^2)$	115°56'	128°08'	2,285	2,489	2,440
$sd_{z^2}f_{yz^2}$	90°	180°	2,403	2,179	1,294
$sd_{z^2}f_y(x^2-y^2)$	90°	180°	2,403	2,513	2,102
$sd_{x^2-y^2}f_{yz^2}$	90°	180°	2,158	2,513	2,017
$sd_{x^2-y^2}f_y(x^2-y^2)$	90°	180°	2,158	2,847	2,825
$sf_{xz^2}d_{xy}$	139°30'	81°	1,900	2,433	1,599
$sf_{x(x^2-y^2)}d_{xy}$	126°15'	107°30'	2,285	2,692	2,642
$p_xp_yd_{z^2}$	129°15'	101°30'	1,913	2,037	0,287
$p_xp_yd_{x^2-y^2}$	103°05'	153°50'	2,581	2,129	1,439
$p_xp_yf_{x^2-y^2}$	121°34'	116°52'	2,707	2,411	1,974
$p_xd_{z^2}d_{xy}$	141°33'	76°54'	1,913	2,573	1,155
$p_xd_{x^2-y^2}d_{xy}$	154°10'	51°40'	2,581	2,466	1,909

In a number of cases the analytical expressions found for hybrid orbits may be combined in various ways : a) by comparing the separate combinations of σ -functions, belonging to some unreduced representation, with the separate atomic orbits of this representation, and b) by comparing the normalized linear combinations of atomic orbits, belonging to the given unreduced representation, with various combinations of σ -functions.

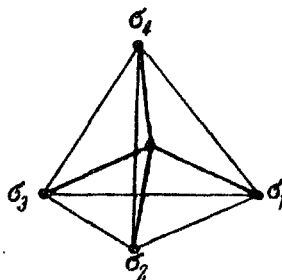
At c.n. 2, sp and sd hybridization results only in a linear (sp) and angular (sd) disposition of the bonds. In sf, dp, and df hybridization, an angular and a linear disposition of the bonds is possible. However, $sf_{z^2} \cdot d_{z^2}pz$ and $d_{z^2}f_{z^2}$ hybridizations, corresponding to $D_{\infty h}$ symmetry, result in considerable strengthening of the bonds. Angular disposition is not favored, as it results in either low or negative values of Δ . Of all the possible fp hybridizations, only $f_{xz^2}pz$ ($\Delta = 1.313$) and $p_xf_{z^2}(x^2-y^2)$ ($\Delta = 0.850$) give positive values of Δ . The hybridization $f_{xz^2}pz$ is also more probable due to the large valence angle. The possible hybridizations d^2 and f^2 result in little strengthening of the bonds. The most advantageous hybridizations are $d_{x^2-y^2}d_{xz}$ ($\Delta = 0.558$) and $f_{xz^2}f_{z^2}(x^2-y^2)$ ($\Delta = 0.941$).

As a rule, at c.n. 3, higher symmetry results in greater strengthening of the bonds, though in this case there are examples when Δ has a maximum value at lower symmetry. For example, with dp^2 - and sf^2 -electrons, Δ is much greater with C_{2v} symmetry than with D_{3h} symmetry and it is precisely this phenomenon which apparently

Coordination Number 4
 T_d symmetry (Fig. 6)

$$\sigma_{1,2} = \frac{1}{2} (a \pm b + c \pm d)$$

$$\sigma_{3,4} = \frac{1}{2} (a \pm b - c \mp d)$$

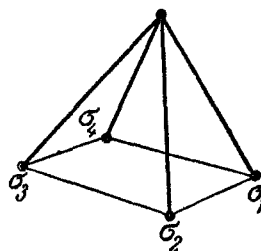


Hybridization	Angles between the directions of the maximum values of hybrid functions	M	Δ
$sp_z p_x p_y$	$109^\circ 28'$	2,000	1,804
$sd_{xz} d_{yz} d_{xy}$	$109^\circ 28'$	2,436	2,936
$f_{xyz} p_z p_x p_y$	$109^\circ 28'$	2,484	2,768
$f_{xyz} d_{xz} d_{yz} d_{xy}$	$109^\circ 28'$	2,921	3,904

C_{4v} symmetry (Fig. 7)

$$\sigma_{1,2} = \frac{1}{2} (a \pm b + c \pm d)$$

$$\sigma_{3,4} = \frac{1}{2} (a \pm b - c \mp d)$$



Hybridization	Angles between the directions of the maximum values of hybrid functions	M	Δ
$sd_{xy} d_{xz} d_{yz}$	$70^\circ 31'$	2,436	2,936
$sf_{xyz} p_x p_y$	$75^\circ 58'$	2,522	3,652
$sf_{xyz} d_{xz} d_{yz}$	$65^\circ 35'$	2,815	4,416
$sf_{xyz} f_{xz^2} f_{yz^2}$	$58^\circ 38'$	2,658	3,198
$sf_{xyz} f_{z(x^2-y^2)} f_{y(x^2-y^2)}$	$82^\circ 10'$	2,504	2,861
$d_{z^2} d_{xy} d_{xz} d_{yz}$	$51^\circ 28'$	2,178	0,668
$p_z p_x p_y d_{xy}$	$85^\circ 48'$	2,310	2,108
$p_z d_{xy} d_{xz} d_{yz}$	$63^\circ 42'$	2,476	,364
$p_z d_{xy} f_{xz^2} f_{yz^2}$	$45^\circ 08'$	2,704	2,686

explains why ClF_3 , in which the bonds are formed from the $p^2 d^2$ -electrons of chlorine in an excited trivalent state

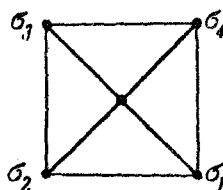
($s^2 p^4 d$), has a T-shape $\begin{array}{c} F \\ | \\ F-Cl-F \end{array}$ with two valence angles of 90° and one of 180° (C_{2v} symmetry) and not a

more symmetrical configuration with D_{3h} symmetry. The hybridizations dsp and fds result in considerable strengthening. In these cases the most advantageous hybridizations are those when two of the directions of maximum concentration of valence orbits are linear and the third is perpendicular to them. Such a configuration is possible

D_{4h} symmetry (Fig. 8)

$$\sigma_{1,2} = \frac{1}{2} (a \pm b + c \pm d)$$

$$\sigma_{3,4} = \frac{1}{2} (a \pm b - c \mp d)$$



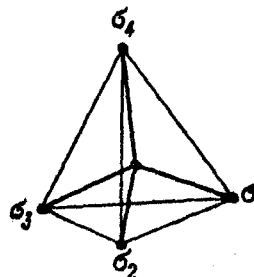
Hybridization	Angles between the directions of the maximum values of hybrid functions	M	Δ
$sd_{xy}^{\pi} p_x p_y$	90°	2,693	4,372
$sd_{xy} f_{xz^2} f_{yz^2}$	90°	2,614	3,057
$sd_{xy} f_x (x^2 - y^2) f_y (x^2 - y^2)$	90°	2,571	3,165

Симметрия C_{3v} (Фиг. 9)

$$\sigma_4 = \frac{1}{2} a + \frac{\sqrt{3}}{2} b$$

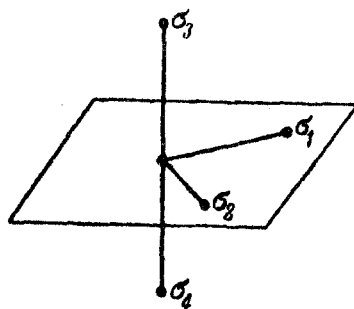
$$\sigma_2 = \frac{1}{2} a - \frac{1}{2\sqrt{3}} b + \frac{2}{\sqrt{6}} c$$

$$\sigma_{2,3} = \frac{1}{2} a - \frac{1}{2\sqrt{3}} b - \frac{1}{\sqrt{6}} c \pm \frac{1}{\sqrt{2}} d$$



Hybridization	Angles between orbits		M		Δ
	$\begin{matrix} \sigma_4 \sigma_2 \\ \sigma_4 \sigma_3 \\ \sigma_4 \sigma_1 \end{matrix}$	$\begin{matrix} \sigma_2 \sigma_1 \\ \sigma_3 \sigma_1 \\ \sigma_1 \sigma_2 \end{matrix}$	σ_4	$\sigma_2 \sigma_3 \sigma_4$	
$sp_z d_{xz} d_{yz}$	136°21'	73°26'	2,0	2,441	2,719
$sp_z d_{xy} d_{x^2-y^2}$	99°06'	117°32'	2,0	2,120	2,756
$sd_{z^2} p_x p_y$	90°	120°	2,436	2,237	2,447
$sd_{z^2} d_{xz} d_{yz}$	126°29'	87°20'	2,436	1,992	1,304
$sd_{z^2} d_{xy} d_{x^2-y^2}$	90°	120°	2,436	2,404	2,540
$sp_z f_{xz^2} f_{yz^2}$	149°52'	51°32'	2,0	2,752	3,062
$sp_z f_z (x^2 - y^2) f_{xyz}$	122°50'	93°22'	2,0	2,373	2,443
$sd_{z^2} f_{xz^2} f_{yz^2}$	90°	120°	2,436	2,146	1,176
$sd_{z^2} f_z (x^2 - y^2) f_{xyz}$	120°19'	96°44'	2,436	2,159	1,733
$sf_{z^2} p_x p_y$	112°35'	106°12'	2,792	2,137	2,093
$sf_{z^2} d_{xz} d_{yz}$	127°40'	86°34'	2,792	2,294	2,156
$sf_{z^2} d_{xy} d_{x^2-y^2}$	104°27'	113°58'	2,792	2,238	1,988
$sf_{z^2} f_{xz^2} f_{yz^2}$	154°40'	43°30'	2,792	2,505	2,199
$sf_{z^2} f_z (x^2 - y^2) f_{xyz}$	122°40'	93°36'	2,792	2,418	2,456
$p_z d_{z^2} p_x p_y$	104°46'	113°44'	2,802	1,848	0,914
$p_z d_{z^2} d_{xz} d_{yz}$	156°11'	40°46'	2,802	2,448	2,306
$p_z d_{z^2} d_{xy} d_{x^2-y^2}$	99°46'	117°10'	2,802	1,977	0,893
$p_z f_{z^2} d_{xz} d_{yz}$	130°52'	81°49'	3,157	2,346	1,945
$p_z f_{z^2} d_{xy} d_{x^2-y^2}$	112°12'	106°36'	3,157	2,012	0,943
$d_{z^2} f_{z^2} d_{xz} d_{yz}$	136°17'	72°58'	3,409	2,003	0,664
$d_{z^2} f_{z^2} d_{xy} d_{x^2-y^2}$	115°31'	102°48'	3,409	1,877	0,286

$$\begin{aligned} a) \sigma_{1,2} &= \frac{1}{\sqrt{2}}(a \pm c) & c) \sigma_{1,2} &= \frac{1}{2} a + \frac{1}{2} b \pm \frac{1}{\sqrt{2}} c \\ \sigma_{3,4} &= \frac{1}{\sqrt{2}}(b \pm d) & \sigma_{3,4} &= \frac{1}{2} a - \frac{1}{2} b \pm \frac{1}{\sqrt{2}} d \end{aligned}$$



Hybridization	Angles between the directions of the maximum values of hybrid functions		M		Δ
	$\sigma_1\sigma_2$	$\sigma_3\sigma_4$	$\sigma_1\sigma_3$	$\sigma_2\sigma_4$	
$sd_{x^2-y^2}d_{xz}p_y$	a) 90°	180°	2,076	2,594	2,736
	c) 70°31'	180°	2,436	2,693	3,654
$sp_xd_{xz}d_{xy}$	78°28'	78°28'	2,512	2,512	3,444
$sd_{z^2}p_zd_{xy}$	180°	90°	2,842	2,428	3,636
$sd_{z^2}d_{xz}p_y$	121°30'	180°	2,385	2,292	2,450
$sd_{x^2-y^2}p_zd_{xy}$	78°28'	45°	2,024	2,153	1,750
$sp_xd_{xz}f_{yz^2}$	78°28'	105°50'	2,512	1,936	1,997
$sp_xf_{xz}d_{xy}$	171°08'	78°28'	2,404	2,512	2,518
$sd_{z^2}f_{z^2}d_{xy}$	180°	90°	3,489	2,428	4,016
$p_xd_{z^2}p_zp_y$	a) 180°	90°	2,806	1,732	1,644
	c) 158°20'	109°28'	2,424	2,059	1,534
$p_xd_{x^2-y^2}p_zp_y$	90°	180°	1,732	2,594	1,520
$p_xd_{z^2}d_{xz}d_{xy}$	130°53'	74°20'	2,209	2,294	1,166
$p_xd_{x^2-y^2}d_{xz}d_{xy}$	63°26'	74°20'	2,215	2,294	1,478
$d_{z^2}d_{x^2-y^2}p_zd_{xy}$	180°	45°	2,806	1,936	1,644
$d_{z^2}d_{x^2-y^2}d_{xz}p_y$	130°53'	180°	2,209	2,594	1,766
$d_{z^2}d_{x^2-y^2}d_{xz}d_{xy}$	90°	63°26'	2,160	2,215	0,706
$p_xd_{z^2}p_zf_y(x^2-y^2)$	180°	55°06'	2,806	2,553	2,927
$p_xd_{z^2}f_{z^2}p_y$	180°	90°	3,450	1,732	2,018
$p_xd_{x^2-y^2}p_zf_y(x^2-y^2)$	90°	180°	1,732	2,849	1,671
$d_{z^2}f_{xz}p_zp_y$	180°	98°54'	2,806	2,076	1,833
$p_xd_{z^2}f_{z^2}d_{xy}$	180°	74°20'	3,450	2,294	2,938
$d_{x^2-y^2}f_{xz}d_{xz}p_y$	180°	98°08'	2,594	2,752	2,857
$d_{z^2}f_{xz}f_{z^2}f_y(x^2-y^2)$	180°	55°24'	3,450	2,483	2,662
$d_{z^2}f_x(x^2-y^2)f_{z^2}f_{yz^2}$	180°	110°	3,450	2,367	2,430

for trivalent compounds of Cu, Ag, and Au, and for Se and I if, in the excited state, they have one d^- , one s^- and one p^- valence electron.

Of the four possible spf hybridizations leading to C_{2v} symmetry, the most advantageous hybridizations are those which are composed of s , p_x , $f_y(x^2-y^2)$ and s , p_y , $f_x(x^2-y^2)$ valence electrons. In these cases the valence angles between the maximum directions of the hybrid functions are also favored. The most advantageous fdp hybridization is $p_xd_{x^2-y^2}f_y(x^2-y^2)$.

With the coordination number 4, the electron configurations sp^3 , d^3s , fp^3 , fd^3 result in a tetrahedral disposition of the directions of the maximum values of the valence orbitals; d^3s , fp^3 and fd^3 orbitals may also give hybrid orbitals with the symmetries C_{4v} , C_{3v} and C_{2v} but Δ is maximum with T_d symmetry. Δ is maximal with D_{4h} symmetry

for the electron configurations dsp^2 and f^2ds . With the electron configurations dp^3 , d^3p , fsp^2 , fd^2s , f^2dp , f^2p^2 , fdp^2 , f^3d , fd^2p , f^3p , which may result in C_{3v} , C_{4v} , and C_{2v} symmetries, Δ is appreciably greater for C_{4v} and C_{2v} than for C_{3v} . The data obtained indicate that an irregular tetrahedral configuration is not favored. With one f-, one d-, one p-, and one s-electron, the maximum concentration of hybrid orbits forms a configuration with only C_{2v} symmetry. Of the possible hybridizations $sp^3f^2d^2xy$ gives maximum Δ .

With hybridization of four d-electrons, the maximum concentrations of hybrid orbits are directed towards the base angles of a four-faced pyramid or form a configuration with C_{2v} symmetry. As the difference in Δ is so small (0.668 with C_{4v} symmetry and 0.706 with C_{2v} symmetry) it is difficult to choose between these configurations. Both configurations have disadvantages with respect to valence angles.

SUMMARY

1. Analytical expressions for hybrid orbits at coordination numbers of 2, 3, and 4 and C_{2v} , $D_{\infty h}$, D_{3h} , C_{3v} , T_d , C_{4v} , D_{4h} symmetries were obtained.
2. From the analytical expressions we found the directions of maximum concentrations and maximum values of hybrid functions. A comparison of the sums of maximum values of the functions is an approach to solving the problem of the selection of symmetry.
3. We calculated the values of the angles between the directions of maximum concentrations for symmetries which are compatible with various valence angles.

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