Chemical Applications of Topology and Group Theory. 31. Atomic Orbital Graphs and the Shapes of the g and h Orbitals[1]

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Atomic orbitals, which are described by the quantum numbers n, l, and m, can be depicted by an orbital graph in which the vertices correspond to the lobes of the atomic orbitals and the edges to nodes between adjacent lobes of opposite sign. The orbital graph for the unique orbital with $m = 0$ for a given value of l consists of a linear graph with $l + 1$ vertices. The orbital graphs for the pair of orbitals with $m = \pm l$ consist of polygons with $2l$ vertices. The orbital graphs for the remaining $2(l - 1)$ orbitals with $0 < |m| < l$ consist of a stack of $l + 1 - |m|$ polygons each with $|2m|$ vertices. For a given value of l the atomic orbitals with $|m| = k$ and $|m'| = l + 1 - k$ have the same numbers of lobes. Orbital graphs are useful for understanding not only the shapes of atomic orbitals of high nodality but also the shapes of the molecular orbitals in molecules approximated by a sphere such as the C_{60} fullerene.

1. Introduction

The shapes of the s, p, and d orbitals are very familiar to many chemists and play a major role in understanding the chemistry of both the main group and transition elements. The shapes of the f orbitals are less familiar to chemists but have been documented in the literature[2−5] and become involved in understanding some aspects of actinide chemistry.[6]

Atomic orbitals of higher nodality, namely g and h orbitals, have received very little attention largely because their shapes[7] are not significant in understanding the chemistry of any known chemical elements or even potential future superheavy chemical elements likely to have half-lives long enough to exhibit observable chemistry. This paper presents a graph-theoretical method for understanding the shapes of atomic orbitals of higher nodality and related molecular orbitals described by analogous spherical harmonics. Although such atomic orbitals are of questionable chemical relevance, some molecular orbitals, notably those of the spherical C_{60} fullerene, have the same shapes and angular dependences as the higher nodality atomic orbitals. Thus molecular orbitals of C_{60} corresponding to the 9 atomic g orbitals are filled molecular orbitals whereas those corresponding to the eleven atomic h orbitals are the frontier orbitals.

2. Background

The atomic orbital wave function $\Psi(r,\theta,\phi)$ may be factored into the product

$$\Psi(r,\theta,\phi) = R(r)\cdot\Theta(\theta)\cdot\Phi(\phi) \qquad (1)$$

in which the factors R, Θ, and Φ are functions solely of r, θ, and ϕ, respectively, which are related to the coordinates x, y, and z by the following equations:

$$x = r \sin \theta \cos \phi \qquad (2a)$$

$$y = r \sin \theta \sin \phi \qquad (2b)$$

$$z = r \cos \theta \qquad (2c)$$

All of the symmetry properties of the wave function, Ψ, are contained in its angular component $\Theta(\theta)\cdot\Phi(\phi)$ which is defined

by the spherical harmonics $Y_{lm}(\theta,\phi)$, i.e.

$$\Theta(\theta)\cdot\Phi(\phi) = Y_{lm}(\theta,\phi) \qquad (3)$$

The spherical harmonics $Y_{lm}(\theta,\phi)$ are characterized by the azimuthal quantum number l, corresponding to the number of nodes, and the magnetic quantum number m, corresponding to the tilt of the plane of orbital motion with respect to some reference direction (typically the z axis).[8]

The angular dependence of the spherical harmonics $Y_{lm}(\theta,\phi)$ can be expressed as a homogeneous polynomial $f(x,y,z)$ by converting the angular variables θ and ϕ to the Cartesian variables x, y, and z using eqs 2a, 2b, and 2c, respectively; this polynomial is conveniently called the *orbital polynomial*. The degree of the orbital polynomial equals the number of nodes, i.e., 0, 1, 2, 3, 4, and 5 for s, p, d, f, g, and h orbitals, respectively, and its maximum exponent of z is equal to $l - |m|$. In some cases the expressions for the orbital polynomial in the tables are simplified by using the variable r and the relationship $r^2 = x^2 - y^2$.

A convenient way of depicting the shape of an orbital, particularly complicated orbitals with large numbers of lobes, is by the use of an orbital graph.[9] In such an orbital graph the vertices correspond to the lobes of the atomic orbitals and the edges to nodes between adjacent lobes of opposite sign. Such an orbital graph is necessarily a bipartite graph in which each vertex is labeled with the sign of the corresponding lobe and only vertices of opposite sign can be connected by an edge.

Table 1 illustrates some of the important properties of s, p, and d orbitals. Similarly Table 2 lists some of the important properties of two different sets of seven f orbitals. The cubic set of f orbitals is used for structures of sufficiently high symmetry (e.g., O_h and I_h) to have sets of triply degenerate f orbitals, whereas the general set of f orbitals is used for structures of lower symmetry without sets of f orbitals having degeneracies 3 or higher. Tables 3 and 4 list some of the important properties of the sets of 9 g orbitals, and 11 h orbitals, respectively, which correspond to the general set of f orbitals (Table 2). For clarity only the general form of the orbital graphs are shown in the tables with no attempt being made to align them relative to the Cartesian coordinates x, y, and z. However, Figure 1 shows the orientations of the orbital graphs of the five g orbital types relative to the z axis.

TABLE 1: Properties of s, p, and d Atomic Orbitals

| Type	$|m|$	Nodes	Polynomial	Angular Function	Appearance and Orbital Graph	Shape
s	0	0		independent of θ, ϕ	spherically symmetrical	point
p	1	1	x	$\sin\theta\cos\phi$		linear
p	1	1	y	$\sin\theta\sin\phi$		
p	0	1	z	$\cos\theta$		
d	2	2	xy	$\sin^2\theta\sin 2\phi$		square
d	2	2	x^2-y^2	$\sin^2\theta\cos 2\phi$		
d	1	2	xz	$\sin\theta\cos\theta\cos\phi$		
d	1	2	yz	$\sin\theta\cos\theta\sin\phi$		
d	0	3	$2z^2-r^2$ (abbreviated as z^2)	$(3\cos^2\theta-1)$		linear

TABLE 2: Properties of the f Atomic Orbitals

$|m|$	Lobes	Shape	Orbital Graph	General Set	Cubic Set
3	6	Hexagon		$x(x^2-3y^2)$ $y(3x^2-y^2)$	none
2	8	Cube		xyz $z(x^2-y^2)$	xyz $x(z^2-y^2)$ $y(z^2-x^2)$ $z(x^2-y^2)$
1	6	Double Square		$x(5z^2-r^2)$ $y(5z^2-r^2)$	none
0	4	Linear		$z(5z^2-r^2)$	x^3 y^3 z^3
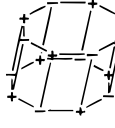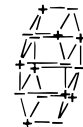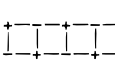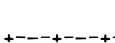
TABLE 3: Properties of the g Atomic Orbitals

$|m|$	Lobes	Shape	Orbital Graph	Polynomial
4	8	Octagon		$x^4+y^4-6x^2y^2$ $xy(x^2-y^2)$
3	12	Hexagonal Prism		$xz(x^2-3y^2)$ $yz(y^2-3x^2)$
2	12	Double Cube		$(x^2-y^2)(7z^2-r^2)$ $xy(7z^2-r^2)$
1	8	Triple Square		$y(7z^3-3zr^2)$ $x(7z^3-3zr^2)$
0	5	Linear		$35z^4-30z^2r^2+3r^4$

TABLE 4: Properties of the h Atomic Orbitals

$|m|$	Lobes	Shape	Orbital Graph	Polynomial
5	10	Decagon		$x^5-10x^3y^2+5xy^4$ $y^5-10x^2y^3+5x^4y$
4	16	Octagonal Prism		$xyz(x^2-y^2)$ $z(x^4+y^4-6x^2y^2)$
3	18	Double Hexagonal Prism		$x(x^2-3y^2)(9z^2-r^2)$ $y(y^2-3x^2)(9z^2-r^2)$
2	16	Triple Cube		$xyz(3z^2-r^2)$ $z(x^2-y^2)(3z^2-r^2)$
1	10	Quadruple Square		$x(21z^4-14z^2r^2+r^4)$ $y(21z^4-14z^2r^2+r^4)$
0	6	Linear		$z(63z^4-70z^2r^2+15r^4)$

Observations

The orbital graph for the unique orbital with $m=0$ for a given value of l consists of a linear graph with $l+1$ vertices oriented along the z axis. The orbital graphs for the pair of orbitals with $m=\pm l$ (i.e., $|m|=l$) are a pair of polygons with $2l$ vertices (i.e., C_{2l} graphs) located in the xy plane. The orbital graphs for the remaining $2(l-1)$ orbitals with $0<|m|<l$ consist of stacks of $l+1-|m|$ polygons each with $2|m|$ vertices.

These polygons are the orbital graphs for the corresponding atomic orbitals with $|m|=l'$ where $l'<l$. In this connection a two-vertex line segment such as the orbital graphs of the p orbitals is considered to be a "polygon" with two vertices, which has been called a *digon*. A stack of two polygons is conventionally called a polygonal prism, a stack of three polygons is called a double polygonal prism, etc. A square prism is a cube. A stack of two digons becomes a square (i.e., a "digonal prism"), whereas a stack of three digons becomes a double square, (i.e., a "double digonal prism"), etc. All orbital graphs generated by this procedure are necessarily bipartite graphs; i.e., their vertices can be labeled with plus or minus signs so that every edge connects a plus vertex to a minus vertex. Furthermore, every vertex of an orbital graph for orbitals with $m\neq 0$ is part of at least one cycle of even length (i.e., a square, hexagon, octagon, etc.).

The numbers of lobes in atomic orbitals with $|m|\neq 0$ for a given value of l follow a pattern that can be seen from the numbers of vertices of the corresponding orbital graphs. Thus the atomic orbitals where $|m|=k$ and $|m'|=l+1-k$ $(0<k\leq l)$ for a given value of l have the same numbers of lobes so that these values of $|m|$ can be regarded as complementary and the corresponding sets of atomic orbitals can be designated as complementary orbitals. The simplest examples of complementary orbitals are the d(xy) and d(x^2-y^2) orbitals with $|m|=2$ and the d(xz) and d(xy) orbitals with $|m'|=l+1-2=2+1-2=1$, which all have four lobes (Table 1). In this case all of the orbital graphs have the same topologies, namely squares. In more complicated cases the orbital graphs for complementary orbitals still have the same numbers of vertices but different topologies. Thus, in the set of general f orbitals, the f$(x(x^2-3y^2))$ and f$(y(3x^2-y^2))$ orbitals with $|m|=3$ are complementary to the f$(x(5z^2-r^2))$ and f$(y(5z^2-r^2))$ orbitals with $|m'|=l+1-3=3+1-3=1$ and all four of these f orbitals have six lobes. However, the orbital graphs of the f orbitals with $|m|=3$ are hexagons whereas those of the f orbitals with $|m|=1$ are double squares (Table 2).

AO Graphs and Shapes of g and h Orbitals

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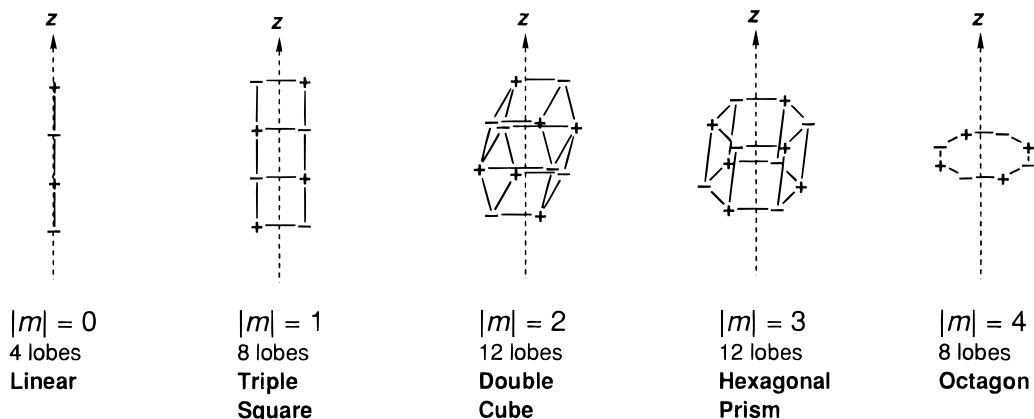| $|m| = 0$	$|m| = 1$	$|m| = 2$	$|m| = 3$	$|m| = 4$
4 lobes	8 lobes	12 lobes	12 lobes	8 lobes
Linear	**Triple Square**	**Double Cube**	**Hexagonal Prism**	**Octagon**

Figure 1. Orbital graphs of the five types of the nine g orbitals oriented relative to the z axis showing the effect of changes in the magnetic quantum number $|m|$.
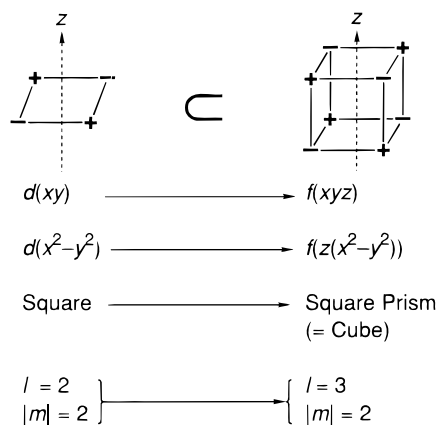

Figure 2. Relationship between the $d(xy)$ and $d(x^2-y^2)$ orbitals ($l = 2$ amd $|m| = 2$) with square orbital graphs and the $f(xyz)$ and $f(z(x^2-y^2))$ orbitals ($l = 3$ and $|m| = 2$) with cube orbital graphs.

The reason for the numbers of vertices in orbital graphs being equal for complementary orbitals can be seen from the way that orbital graphs are constructed. Thus the orbital graphs for orbitals with $0 < |m| < l$ consist of stacks of $l + 1 - |m|$ polygons each with $2|m|$ vertices. If $|m| = k$, the number of vertices in this graph can be expressed by the following equations where v is the total number of vertices in the orbital graph, p is the number of vertices in the polygons being stacked, and h is the height of the stack (i.e., the number of polygons in the stack so that $h = 2$ for prisms, $h = 3$ for double prisms, etc.):

$$v = ph = (2k)(l + 1 - k) = 2kl - 2k^2 + 2k \quad (4)$$

However, for the complementary set of atomic orbitals $k' = l + 1 - k$ so that

$$v' = p'h' = (2[l + 1 - k])(l + 1 - [l + 1 - k])$$

$$= 2(l + 1 - k)k = 2kl - 2k^2 + 2k \quad (5)$$

and $v = v'$.

The form of the orbital polynomial can be related to the shape of the corresponding atomic orbital and its orbital graph. Thus for atomic orbitals with $0 < |m| < l$, the orbital graph consists of a stack of the polygonal orbital graphs of the corresponding atomic orbital with $|m| = l'$ where $l' < l$. Thus Figure 2 considers the $f(xyz)$ and $f(z(x^2-y^2))$ orbitals (Table 2) with $l = 3$ and $|m| = 2$, whose orbital graphs are cubes. These cubes are derived by stacking two squares corresponding to the orbital graphs of the $d(xy)$ and $d(x^2-y^2)$ orbitals with $l = 2$ and $|m| =$
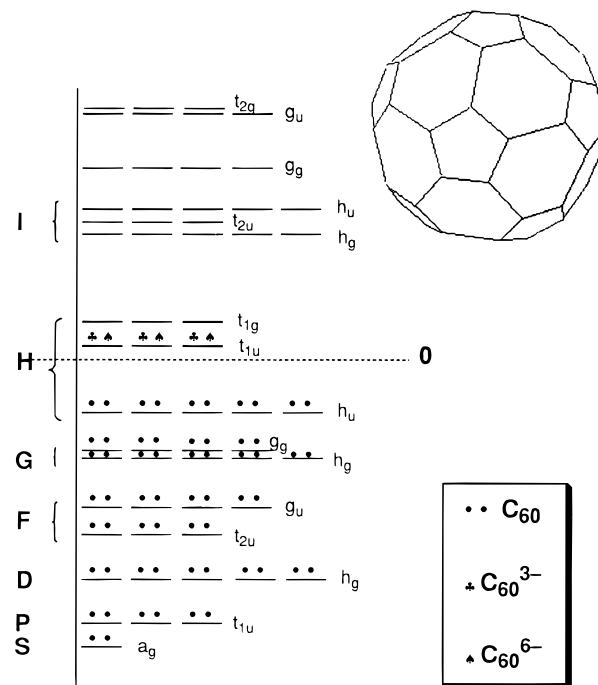

Figure 3. Calculated molecular orbitals energies for C_{60} related to the spherical harmonics with $0 \leq l \leq 6$ designated as S, P, D, F, G, H, and I molecular orbitals, respectively. The 60 electrons for neutral C_{60} are indicated by ●. The additional 3 electrons of C_{60}^{3-} and the additional 6 electrons of C_{60}^{6-} in the triply degenerate t_{1u} molecular orbital of the 11-orbital H frontier orbital manifold are indicated by cloverleaf and by the cloverleaf + spade symbols, respectively.

2. The corresponding orbital polynomials of the d(xy) and d(x^2-y^2) orbitals are seen to be factors of the orbital polynomials of the f(xyz) and f($z(x^2-y^2$)) orbitals (Figure 2).

Possible Applications

The g and h atomic orbitals, although they have intriguing shapes, do not appear to be relevant to the chemistry of any element expected to be synthesized and isolated. However, orbitals shaped like g and h orbitals can appear in species approximated by spherical symmetry leading to *molecular* orbitals resembling spherical harmonics. The most interesting case is the C_{60} truncated icosahedral fullerene (Figure 3) which can be approximated by a sphere. The filled molecular orbitals of C_{60} include not only one S (a_g), three P (t_{1u}), five D (h_g), and seven F ($t_{2u} + g_u$) orbitals but also nine G ($h_g + g_g$) orbitals. Furthermore, the nine G orbitals are calculated[10] to be degenerate in an *ideal* truncated icosahedron corresponding to the C_{60}
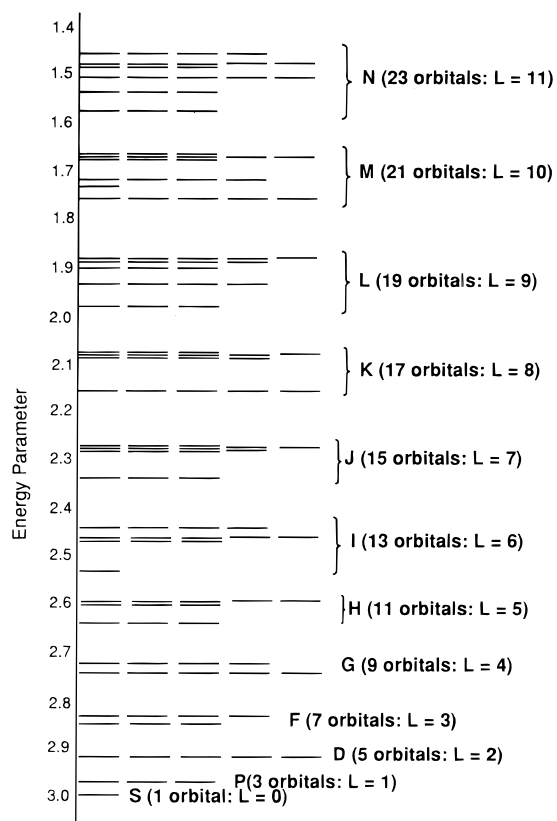
Figure 4. Lowest lying molecular orbitals calculated[12] for C_{540} plotted according to their energy parameters showing orbitals up to those with 11 nodes (designated as N orbitals in an extension of the S, P, D, F,... designations).

structure. Up to this point the parities of the C_{60} molecular orbitals alternate in the sequence S → P → D → F → G as

expected corresponding to the parity of the number of nodes. The frontier orbitals of C_{60} are the 11 H orbitals with up to 8 of the H orbitals being filled in the hexaanion C_{60}^{6-} (Figure 3). Higher spherical fullerenes,[11-14] are likely to provide examples of higher nodality molecular orbitals than even the H orbitals of C_{60}. Thus Figure 4 provides an illustration of the lowest lying higher nodality molecular orbitals up to $L = 11$ calculated[12] for the hypothetical large spherical fullerene C_{540} of icosahedral symmetry belonging to the C_n, $n = 60(\nu + 1)^2$ family ($n = 2$) of giant fullerenes.[13,14] Note how the molecular orbitals in Figure 4 are bunched according to their energy parameters in groups of $2L + 1$ molecular orbitals. Further details on the relationship of the molecular orbital patterns of the C_{60n^2} fullerenes to spherical harmonics are presented elsewhere.[15]

References and Notes

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