

# Bond and Structure Models 63

With Contributions by  
J. C. A. Boeyens S. N. Bose J. C. Hawes  
D. M. P. Mingos K. Nag S.-C. Tam  
R. J. P. Williams

With 66 Figures and 39 Tables

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# Complementary Spherical Electron Density Model

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The bonding in inorganic molecules of the main group and transition metals is discussed in terms of a model which accounts simultaneously for their stereochemistries and their adoption of the inert gas counting rules. A molecular compound can be viewed initially as a central atom surrounded by a spherical shell of electron density, which is representative of the ligand co-ordination sphere. Since the wave functions for this spherical shell are derived from the particle on a sphere problem it is an easy matter to define the conditions for the inert gas rule in this hypothetical situation, because the wave functions for the sphere and the central atom are both expressed in terms of spherical harmonics with identical quantum numbers. The linear combinations of ligand orbitals in a real complex can be expressed as spherical harmonic expansions and their nodal characteristics defined by the same quantum numbers. Only co-ordination polyhedra where the atoms provide effective coverage or packing on the sphere generate linear combinations in the sequential fashion S, P, D, etc.. These orbitals interact in a complementary fashion with the valence orbitals of the central atom to give a complete set of molecular orbitals, which emulate those of an inert gas in number and nodal characteristics. This Complementary Spherical Electron Density Model thereby provides an effective way of accounting for the stereochemistries of main group and transition metal compounds.

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









## A. Introduction

Understanding the factors which influence the shapes of inorganic molecules represents an on-going challenge for quantum mechanics. The difficulty of providing exact quantum mechanical solutions for chemical systems of interest has meant that this stereochemical problem has had to be approached using approximate methods, none of which has proved to be totally satisfactory. The common occurrence of stable electronic configurations related to those of the inert gases was utilised by Lewis initially and subsequently extended by Sidgwick to formulate the inert gas rule<sup>1,2</sup>. Although this rule generally defined the stoichiometries of many chemical compounds, it did not provide three dimensional stereochemical descriptions of their structures.

It was Pauling<sup>3</sup> who was able to develop an approximate quantum mechanical model based on the Valence Bond Theory which successfully rationalised the shapes of simple organic, inorganic and co-ordination compounds in terms of hybrid orbitals on the central atom. This localised view of bonding represented a quantum mechanical description of the electron pair bond concept developed by Lewis. Furthermore when combined with the concept of resonance it had a profound and important impact on the development of organic and inorganic chemistry throughout the nineteen forties and fifties<sup>4</sup>. The valence bond method could not be applied in an economical fashion to electron deficient, odd-electron and organo-transition metal  $\pi$ -complexes<sup>5</sup>.

The Sidgwick-Powell approach which was extended and popularised by Nyholm and Gillespie in the nineteen fifties<sup>6,7</sup>, focused attention on the total number of electron pairs surrounding the central atom in a molecule. The idea that electron pairs would tend













Table 1a. Summary in a matrix form of the stereochemistries of main group molecular compounds

$n, N$	7	6	5	4	3	2
$sp^3d^2$	 $IF_7$	 $IOF_5$	 $SOF_4$	 $CH_4, SNF_4$	 $BF_3$	 $BeF_2$
$sp^3d$			 $BrF_5$	 $SiF_4$	 $CH_3, IO_3^-$	 $SO_2$
$sp^3$				 $XeF_4$	 $ClF_3$	 $SeH_2, XeO_2$
$sp$						 $XeF_2$

to occupy regions of space as widely separated as possible had a classical pictorial simplicity and led to a number of preferred co-ordination polyhedra. This approach emphasised the fact that the shapes of main group inorganic molecules could be understood in terms of a small number of easily defined rules despite the apparent complexity of the quantum mechanical problem. For example, since there is a relationship between the number of electron pairs and deltahedral co-ordination polyhedra the shapes of simple inorganic molecules can be represented in a matrix form such as that shown in Table 1a<sup>8)</sup>. Particularly noteworthy is the manner in which lone pairs successively replace vertices of the parent polyhedra when they exceed the number of ligands. Some theoretical justification for the approach has been obtained from the Pauli Exclusion principle<sup>9)</sup>, but the proposed relative magnitudes for the electron repulsion effects have not found support in modern quantum mechanical calculations<sup>10)</sup>. Furthermore, the method is not readily applicable to transition metal co-ordination compounds (Table 1b), sandwich compounds and polyhedral inorganic molecules.

As a result of the availability of high speed computers the molecular orbital method has been used with increased frequency to solve stereochemical problems. The most popular approach for defining the preferred ground and excited state geometries depends on taking sections through the multi-dimensional potential energy surface and examining how the orbital energies and total energies vary as a function of distortion co-ordinates<sup>11)</sup>. This Walsh diagram methodology<sup>12)</sup> has proved to be widely applicable and reliable and in recent years has been most effectively popularised by Hoffmann and his coworkers<sup>13)</sup>. The reasons why the method works so well even when used in conjunction with crude semi-empirical calculations has puzzled theoretical chemists and suggests the presence of an underlying fundamental principle<sup>14)</sup>. In spite of its notable successes this approach has

Table 1b. Summary of the stereochemistries of transition metal molecular compounds

$n_e \backslash N$	7	6	5	4	3	2
18	 $[\text{Mo}(\text{CN})_7]^{5-}$	 $\text{Cr}(\text{CO})_6$	 $\text{Fe}(\text{CO})_5$	 $[\text{Ni}(\text{CN})_5]^{3-}$	 $\text{Ni}(\text{CO})_4$	
16			 $\text{Cr}(\text{CO})_5$	 $[\text{Ni}(\text{CN})_4]^{2-}$	 $\text{Pt}(\text{PPh}_3)_3$	
14				 $\text{Cr}(\text{CO})_4$	 $[\text{Rh}(\text{PPh}_3)_3]^+$	 $[\text{Ag}(\text{NH}_3)_2]^+$
12					 $\text{Cr}(\text{CO})_3$	

pedagogical limitations since it requires the consideration of many distortion co-ordinates before sensible choices concerning the relative stabilities of alternative geometries can be made.

Above we have noted the historical development of the more important approaches to the stereochemical problem. References 15 and 16 summarise some alternative approaches which have been described. Although familiarity with any one of the major approaches described above can make them into powerful tools for the chemist, pedagogically the situation is far from satisfactory. To the simple and fundamental chemical question "What determines the shapes of molecules?" there is no intellectually satisfactory answer. The valence bond method associates preferred geometries to superior overlap effects, the valence shell electron pair repulsion theory depends on maximising the distances between electron pairs and the Walsh methodology depends on very specific arguments associated with energy changes of specific molecular orbitals along the distortion co-ordinate.

In this review we develop a new stereochemical model, – *The Complementary Spherical Electron Density Model*. This model views molecules as interpenetrating spheres of electron density, and attempts to unify the inert gas rule and molecular orbital formalisms. It depends critically on the ideal that the wave functions of ligands can be expressed in terms of spherical harmonics. This idea can be traced back to a paper by Verkade et al.<sup>17)</sup>, but the recent analysis by Stone of cluster compounds using this methodology was particularly formative<sup>18)</sup>. The importance of this concept has also been noted by Quinn<sup>19)</sup>, who has described a useful method of illustrating spherical, vector spherical and tensor spherical harmonic functions as projections.

## B. Spherical Harmonic Representations of Atomic Orbitals

### I. General Mathematical Considerations

The use of hydrogen-like wavefunctions to describe the electronic properties of atoms is widespread and generally accepted. The wavefunctions are represented as the product of a radial  $R_{n,l}(r)$  and an angular part  $Y_{l,m}(\theta, \phi)$

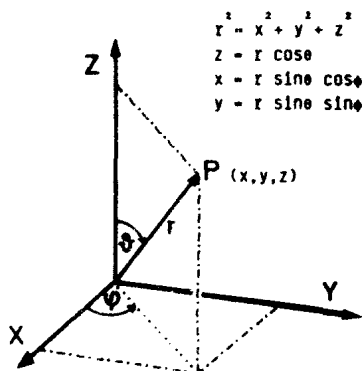


Fig. 1. Definition of spherical polar co-ordinates

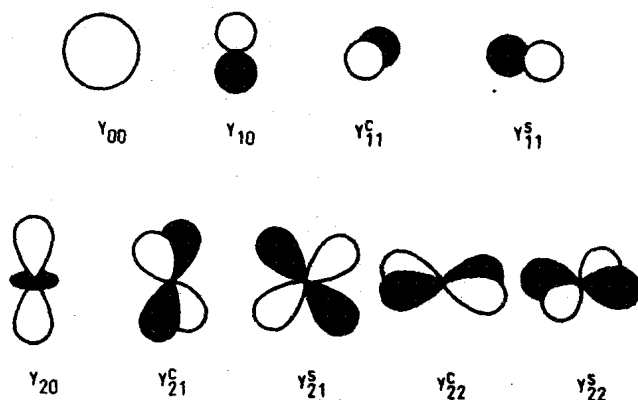
$$\Psi(r, \theta, \phi) = R_{n,l}(r) \cdot Y_{l,m}(\theta, \phi) \quad (I)$$

Where  $r$ ,  $\theta$  and  $\phi$  refer to the spherical polar co-ordinate system illustrated in Fig. 1. The angular part is defined by the spherical harmonic functions given in Table 2. For those functions with imaginary solutions the real solutions are obtained by taking linear combinations of complementary components, i.e.

$$Y_{l,m}^{\pm} = 1/\sqrt{2} [(-1)^m Y_{l,m} \pm Y_{l,-m}] \quad \text{For } m > 0 \quad (II)$$

**Table 2.** Polar forms of the spherical harmonic functions normalised to  $4\pi$

$Y_{l,m}$	Polar Form
$Y_{00}$	1
$Y_{10}$	$\sqrt{3} \cos \theta$
$Y_{11}^c$	$\sqrt{3} \sin \theta \cos \phi$
$Y_{11}^s$	$\sqrt{3} \sin \theta \sin \phi$
$Y_{20}$	$\sqrt{5/4} (3 \cos^2 \theta - 1)$
$Y_{21}^c$	$\sqrt{15} \cos \theta \sin \theta \cos \phi$
$Y_{21}^s$	$\sqrt{15} \cos \theta \sin \theta \sin \phi$
$Y_{22}^c$	$\sqrt{15/4} \sin^2 \theta \cos 2\phi$
$Y_{22}^s$	$\sqrt{15/4} \sin^2 \theta \sin 2\phi$
$Y_{30}$	$\sqrt{7/4} (5 \cos^3 \theta - 3 \cos \theta)$
$Y_{31}^c$	$\sqrt{21/8} \sin \theta (5 \cos^2 \theta - 1) \cos \phi$
$Y_{31}^s$	$\sqrt{21/8} \sin \theta (5 \cos^2 \theta - 1) \sin \phi$
$Y_{32}^c$	$\sqrt{105/4} \cos \theta \sin^2 \theta \cos 2\phi$
$Y_{32}^s$	$\sqrt{105/4} \cos \theta \sin^2 \theta \sin 2\phi$
$Y_{33}^c$	$\sqrt{35/8} \sin^3 \theta \cos 3\phi$
$Y_{33}^s$	$\sqrt{35/8} \sin^3 \theta \sin 3\phi$



**Fig. 2.** Illustration of polar plots of the angular parts of the atomic wavefunctions in their real forms

Figure 2 illustrates the angular parts of the wavefunctions in their real forms for  $s$  ( $l = 0$ ),  $p_z$  ( $l = 1, m = 0$ ),  $p_x$  ( $l = 1, m = 1, c$ ) and  $p_y$  ( $l = 1, m = 1, s$ ),  $d_{z^2}$  ( $l = 2, m = 0$ ),  $d_{xz}$  and  $d_{yz}$  ( $l = 2, m = 1$ ) and  $d_{xy}$  and  $d_{x^2-y^2}$  ( $l = 2, m = 2$ ) atomic orbitals.

The particle on a sphere problem also leads to wave functions which are described in terms of spherical harmonics, but the radial part of the wave function is redundant because the particle is constrained to lie on the surface of the sphere, that is, at a constant radius  $r$ . The spherical harmonic solutions are governed by the same quantum numbers  $l$  and  $m$  and the resultant wave functions can be designated  $S_m$  ( $l = 0$ ),  $P_m$  ( $l = 1$ ) and  $D_m$  ( $l = 2$ ) in an analogous fashion to that adopted for the hydrogen atom.

A molecule can be viewed to a first approximation as a central atom surrounded by a sphere of electron density which has been localised into distinct regions on the sphere. Indeed such a model is the starting point of crystal field theory, where the potential field of an octahedral arrangement of point charges is derived by localising the electron density in just such a manner<sup>20</sup>. In the present analysis, the molecules are covalent and therefore a molecular orbital analysis is more appropriate. In a molecule  $ML_N$  the ligand atomic orbitals are expressed as symmetry adapted linear combinations which combine with the atomic orbitals of the central atom. It is not generally realised, but is very important from the point of view of the present analysis, that it is not necessary to use symmetry arguments to derive ligand linear combinations. As long as the  $N$  atoms are distributed in a spherical fashion about the central atom then the linear combinations can be derived to a first approximation from a spherical harmonic expansion. For example, in  $MH_N$  if the hydrogen atoms are distributed spherically about  $M$  then the symmetry adapted linear combinations  $\psi_{l,m}$  of hydrogen  $1s$  functions,  $\sigma_i$ , can be expressed in terms of the following spherical harmonic expansion:

$$\psi_{l,m} = \sum_i c_i \sigma_i \quad (III)$$

$$= N' \sum_i Y_{l,m}(\theta_i, \phi_i) \cdot \sigma_i \quad (IV)$$

$$= L_m^{\sigma} \quad m = 0, 1c, 1s, \dots \quad L = S, P, D, \dots$$

where  $\theta_i$  and  $\phi_i$  represent the locations of the hydrogen nuclei in spherical polar coordinates (see Fig. 1) and  $N'$  is a normalising constant. In this fashion the linear combinations are assigned quantum numbers  $l$  and  $m$  which are related to those which have been defined previously for  $S$ ,  $P$  and  $D$  functions derived for the particle on the sphere problem. Furthermore, their nodal characteristics mimic those of the atomic wave functions of the central atom,  $M$ . The designation of  $l$  and  $m$  quantum numbers to symmetry adapted linear combinations of ligand orbitals can be traced back to Verkade et al.<sup>17</sup>. It has been formulated in a general mathematical fashion and extended to cluster compounds by Stone<sup>18</sup>. The spherical harmonic expansion described above will provide its most accurate description of the symmetry adapted linear combinations when the ligand polyhedron is a Platonic solid, i.e. tetrahedral, cubic, octahedral, etc. because in those circumstances the polyhedral vertices are symmetry equivalent. It will improve as an approximation as  $N$  increases. For smaller polyhedra it is more of an approximation. When there is more than one linear combination with the same symmetry then there can in addition be normalisation problems. The following section describes the utilisation of these spherical harmonic expansions for a range of ligand co-ordination geometries in order to evaluate the types of  $S^{\sigma}$ ,  $P^{\sigma}$ ,  $D^{\sigma}$  and  $F^{\sigma}$  functions generated.

## II. Planar $MH_N$ Stereochemistries

Figure 3 illustrates schematically the linear combinations of atomic orbitals for some planar  $H_N$  aggregates, together with their Stone designations. Clearly these are non-spherical, but they demonstrate the way in which the  $S^\sigma$ ,  $P^\sigma$  and  $D^\sigma$  functions develop as  $N$  increases. The linear  $H_2$  moiety has a symmetric,  $S^\sigma$ , and antisymmetric,  $P_{1c}^\sigma$ , pair of linear combinations. The  $H_3$  moiety has  $S^\sigma$  and a pair of singly noded  $P_{1s}^\sigma$  and  $P_{1c}^\sigma$  functions. For  $H_4$  the additional function generated is a  $D$  function, i.e. it is characterised by  $S^\sigma$ ,  $P_{1s}^\sigma$ ,  $P_{1c}^\sigma$  and  $D_{2s}^\sigma$ . Therefore, for planar aggregates of atoms not all of the spherical harmonic functions are utilised. The following functions are systematically excluded:

- (1) Those which possess a nodal plane coincident with the  $xy$  plane of the polygon, viz.  $P_0^\sigma$ ,  $D_{1s}^\sigma$ ,  $F_{2c}^\sigma$  ... etc..
- (2) Those having a form in the  $xy$  plane, which when renormalised is identical to those of spherical harmonic functions with lower  $l$ ,  $m$  quantum numbers, e.g.  $D_0^\sigma$  and  $S^\sigma$ ,  $F_{1c}^\sigma$  and  $P_{1c}^\sigma$  are identical in projection.

The remaining allowed set of two dimensional combinations are  $S^\sigma$ ,  $P_{1c}^\sigma$ ,  $P_{1s}^\sigma$ ,  $D_{2c}^\sigma$ ,  $D_{2s}^\sigma$ ,  $F_{3c}^\sigma$ ,  $F_{3s}^\sigma$  ...  $L_{1,s}^\sigma$  are illustrated in Fig. 4. They correspond to the solution of the Schrödinger equation for the particle on the ring problem, i.e. they are the 'two dimen-

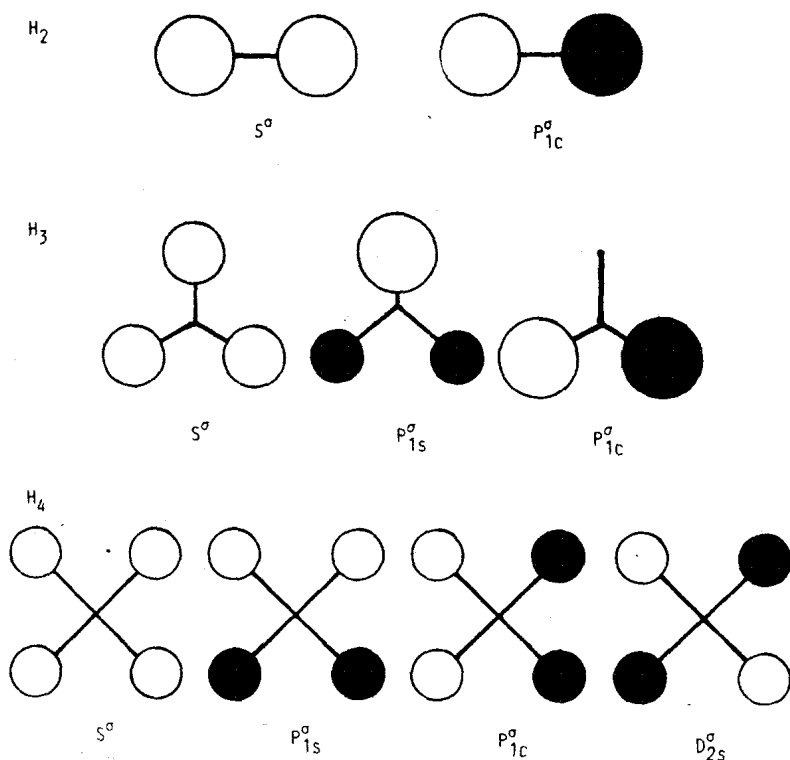


Fig. 3. Schematic representations of the linear combinations,  $L^\sigma$ , for planar aggregates of hydrogen atom 1s functions

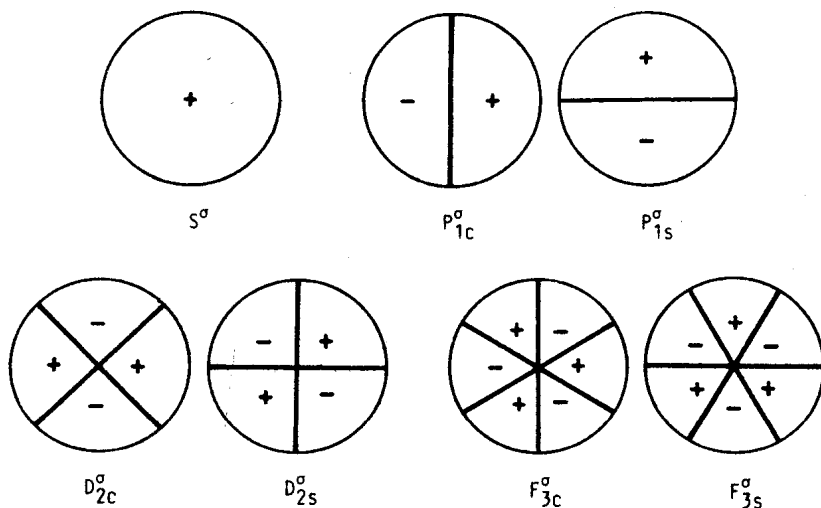


Fig. 4. Schematic representations through the  $xy$  plane of the  $L^\sigma$  functions representing a two dimensional system

Coordination Number	Structure	$S^\sigma$	$P_0^\sigma$	$P_{1c}^\sigma$	$P_{1s}^\sigma$	$D_0^\sigma$	$D_{1c}^\sigma$	$D_{1s}^\sigma$	$D_{2c}^\sigma$	$D_{2s}^\sigma$	$F_0^\sigma$	$F_{1c}^\sigma$	$F_{1s}^\sigma$	$F_{2c}^\sigma$	$F_{2s}^\sigma$	$F_{3c}^\sigma$	$F_{3s}^\sigma$
7	Heptagon	■	■	■	■				■							■	
6	Hexagon	■	■	■	■				■							■	
5	Pentagon	■	■	■	■				■								
4	Square	■	■	■	■				■								
3	Triangle	■	■	■	■												

Fig. 5. Summary of linear combinations for planar  $\sigma$ -donor aggregates and their  $L_m^\sigma$  designators. Particularly noteworthy is the use of  $F^\sigma$  functions when  $N > 5$

sional analogues of the spherical harmonics. Figure 5 illustrates the stepwise manner in which these functions are utilised for planar  $H_N$  aggregates. Particularly noteworthy is the utilisation of  $F$  functions when  $N$  is  $\geq 6$ .

### III. Three Dimensional $MH_N$ Stereochemistries

#### a. Three Connected Polyhedra and Bipyramids

The simplest three dimensional polyhedron is the tetrahedron and the four linear combinations of atomic orbitals ( $S^\sigma$ ,  $P_0^\sigma$ ,  $P_{1c}^\sigma$ ,  $P_{1s}^\sigma$ ) generated from Eq. IV are illustrated in

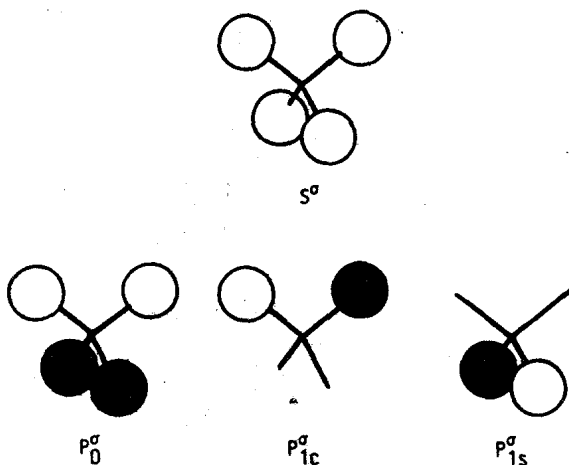


Fig. 6. Linear combinations of 1s orbitals for tetrahedral  $H_4$

Fig. 6. When  $N$  exceeds four then  $D^\sigma$  and even  $F^\sigma$  linear combinations are generated. The particular functions generated depends on the positions of the hydrogen atoms relative to the nodal cones and planes of the  $D$  and  $F$  functions. In this section the spherical harmonic generated linear combinations for bipyramids and three-connected co-ordination polyhedra are explored. The discussion of planar stereochemistries given above has demonstrated that a  $P_0^\sigma$  combination requires the presence of more than one plane of atoms perpendicular to the principle axis. Similarly a  $D_0^\sigma$  function requires at least three planes, an  $F_0^\sigma$  function four planes or more (see Fig. 7). With this property in mind it is possible to understand the occurrence and absence of the  $L_0^\sigma$  linear combinations of ligand orbitals illustrated in Fig. 8 for three connected polyhedra and in Fig. 9 for bipyramids.

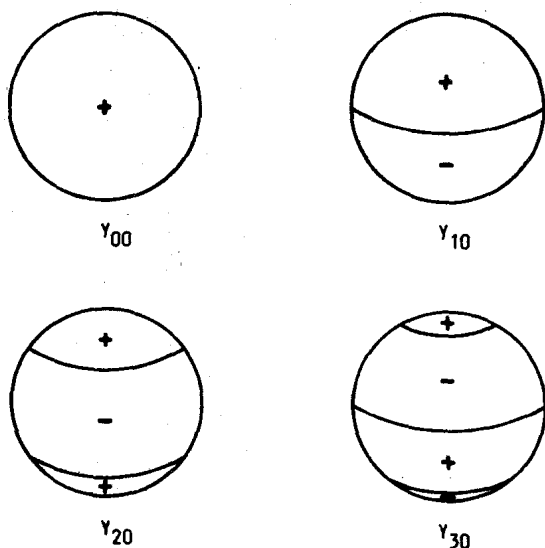


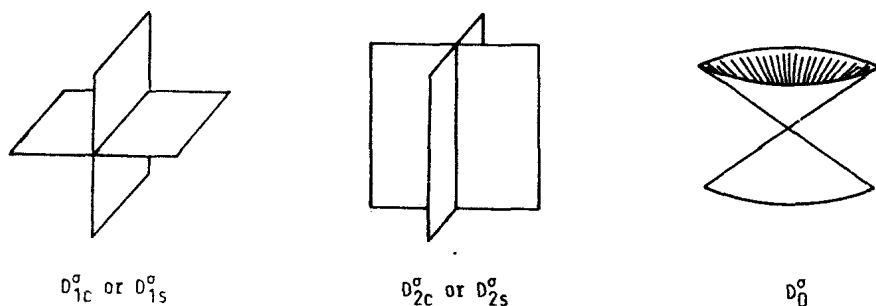
Fig. 7. Nodal characteristics of the cylindrically symmetric  $Y_{l,0}$  spherical harmonics

N	Structure	$S^{\sigma}$	$P_0^{\sigma}$	$P_{1c}^{\sigma}$	$P_{1s}^{\sigma}$	$D_0^{\sigma}$	$D_{1c}^{\sigma}$	$D_{1s}^{\sigma}$	$D_{2c}^{\sigma}$	$D_{2s}^{\sigma}$	$F_0^{\sigma}$	$F_{1c}^{\sigma}$	$F_{1s}^{\sigma}$	$F_{2c}^{\sigma}$	$F_{2s}^{\sigma}$	$F_{3c}^{\sigma}$	$F_{3s}^{\sigma}$
10	Pentagonal Prism																
8	Cube																
6	Trigonal Prism																
4	Tetrahedron																

**Fig. 8.** Summary of linear combinations for three connected co-ordination polyhedra. The absence of  $D_0^{\sigma}$  for all examples is particularly noteworthy

N	Structure	$S^{\sigma}$	$P_0^{\sigma}$	$P_{1c}^{\sigma}$	$P_{1s}^{\sigma}$	$D_0^{\sigma}$	$D_{1c}^{\sigma}$	$D_{1s}^{\sigma}$	$D_{2c}^{\sigma}$	$D_{2s}^{\sigma}$	$F_0^{\sigma}$	$F_{1c}^{\sigma}$	$F_{1s}^{\sigma}$	$F_{2c}^{\sigma}$	$F_{2s}^{\sigma}$	$F_{3c}^{\sigma}$	$F_{3s}^{\sigma}$
9	Heptagonal Bipyramid																
8	Hexagonal Bipyramid																
7	Pentagonal Bipyramid																
6	Octahedron																
5	Trigonal Bipyramid																

**Fig. 9.** Summary of linear combinations for bipyramids.  $D_{1c}^{\sigma}$  and  $D_{1s}^{\sigma}$  are consistently absent



**Fig. 10.** Nodal characteristics of  $D^{\sigma}$  functions

$F^{\sigma}$  linear combinations are generated for  $MH_N$  ( $N = 5-9$ ) when all the hydrogen atoms lie on the nodal cones of  $(10 - N)$  D or P spherical harmonic functions. For example when  $N = 9$ ,  $(10 - N) = 1$ , so at least one  $D^{\sigma}$  function must be excluded if  $F^{\sigma}$  are generated. See Fig. 10 for an illustration of the nodal characteristic of the  $D^{\sigma}$  func-

tions. Location of the atoms along the nodal cones of  $D_0^0$  nullifies this function (all the coefficients,  $c_i$ , are equal to 0) and requires the utilisation of an  $F^0$  function. Similarly location of atoms on the nodal planes of either the  $D_{1c,s}^0$  or  $D_{2c,s}^0$  functions nullifies them and forces the adoption of  $F^0$  functions with an additional nodal plane. See Fig. 11 for a similar analysis of  $N = 8$  and  $N = 7$  polyhedra, where two and three  $L^0$  functions are nullified because of the location of atoms on nodal lines and planes. For example for bipyramids the  $D_{1c}^0$  and  $D_{1s}^0$  functions are always absent, because bipyramids place the equatorial atoms in the horizontal nodal plane of  $D_{1s}^0$  and  $D_{1c}^0$  while the axial atoms always reside in the vertical nodal planes of these functions.

In summary the three-connected polyhedra and bipyramids with  $N > 7$  require the utilisation of  $F^0$  functions in order to account fully for the  $N$  linear combinations of atomic orbitals of the peripheral atoms.

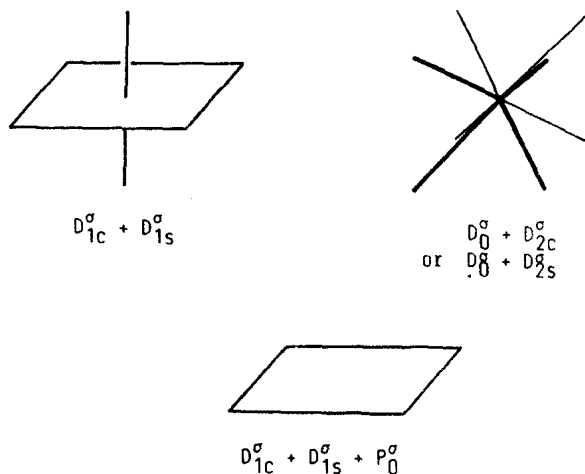


Fig. 11. The nodal characteristics which are common to sets of  $D^0$  and  $P^0$  functions

### b. Deltahedra

Polyhedra with triangular faces exclusively are described as deltahedra and have several interesting geometric properties<sup>21)</sup>. For example, their vertices are connected by the maximum number of edges. This is a property of importance for the borane polyhedra  $B_nH_n^{2-}$ , which are electron deficient and require the maximum degree of delocalisation in order to stabilise the boron skeleton<sup>18)</sup>. Figure 12 gives a detailed analysis of the development of the linear combinations of atomic orbitals for deltahedra and classifies them according to their  $l, m$  quantum numbers. Particularly striking is the sequential fashion in which the linear combinations are built up; unlike the previous classes of polyhedra  $F^0$  functions are not used prior to the completion of the  $D$  shell. This property can be related to the ability of deltahedra to give the best coverage on a sphere, i.e. the most even distribution of points. Consequently, the polyhedra reproduce most closely the surface of the parent spherical shell which surrounds the central atom in  $ML_N$ .

Mathematically this property has been explored previously in the context of the following covering problem by Fejes-Toth and others<sup>22)</sup>.



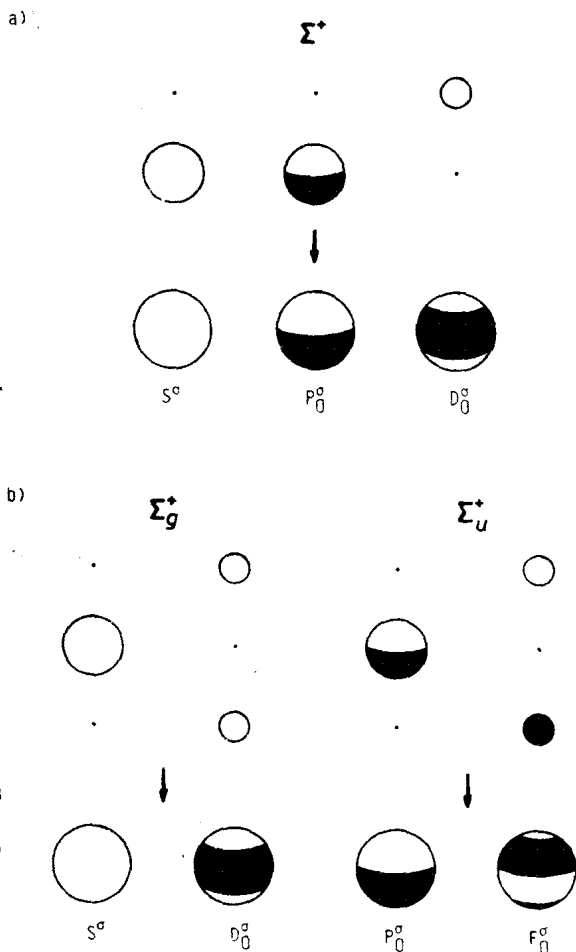
deltahedral arrangement of ligands on a sphere provides a collection of overlapping regions of electron density which most effectively approximate to a spherical shell.

The symmetry properties of the linear combinations of atomic orbitals for deltahedra are summarised in Table 3 and the following characteristics are particularly noteworthy.

The linear combinations have identical symmetry characteristics to those of atomic orbitals located on the central atom and with matching  $l$  and  $m$  quantum numbers. This is a direct consequence of defining both sets in terms of spherical harmonics.

Only for the Platonic solids do  $S^o$ , and  $D_0^o$  functions have different symmetry properties. This is related to the occurrence of cubic fields for these high symmetry polyhedra.

For the polyhedra with  $T_d$ ,  $D_{3h}$  and  $D_{2d}$  symmetries some of the  $P^o$  and  $D^o$  functions have identical symmetry characteristics, e.g.  $P^o(t_2)$  and  $D^o(t_2)$  in  $T_d$ . Therefore, although the  $p$  and  $d$  atomic orbitals for an isolated atom are orthogonal, the corresponding linear combinations  $P^o(t_2)$  and  $D^o(t_2)$  can mix. This arises because the peripheral atoms do not define a perfect sphere and the designation of  $l$ ,  $m$  quantum numbers is only an approxi-



**Fig. 13 a, b.** Schematic illustrations of (a) mono- and (b) bicapping of polyhedral aggregates.  $C_{\infty v}$  and  $D_{\infty h}$  symmetry is assumed to define the symmetry labels. Either one (a) or two (b) new  $L_0^o$  functions are generated respectively