σ, π and δ representations of the molecular point groups

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σ, π and δ representations of the orbits of molecular symmetry groups are tabulated and their mathematical properties discussed. Applications are made to the theory of molecular vibrations, electronic structures of complexes and the tensor surface harmonic theory of bonding in clusters. Attention is drawn to the unified manner in which all these analyses can be carried out using the spherical shell technique.

Key words: Point-group representations — Spherical-shell technique — Clusters — Vibrations

1. Introduction

Group theoretical techniques have found wide application in theories of vibrations and electronic structures of molecules. At the simplest level, they are routinely used to classify normal modes of vibration and molecular orbitals in terms of the point group of the equilibrium nuclear configuration [1]. Orbital symmetries in the three-dimensional rotation group (appropriate to an idealised spherical cluster) can be used to derive a useful, qualitative theory of bonding in clusters [2-5]. A common analysis of all these applications may be based on the σ, π, δ... representations generated by a set of functions on a spherical shell [6-8].

It is the purpose of this paper to tabulate the σ, π and δ representations for all the orbits of the common molecular symmetry groups and to show how they may be used to solve problems in molecular vibrations and electronic structure.

The plan of the paper is as follows. Section 2 sets out the necessary definitions and shows how all higher representations may be derived from the σ or permutation representation. Section 3 describes the tables and comments on some general

properties of the representations. Sect. 4 discusses the application to vibrations of the whole molecule and of groups within it. Sect. 5 shows that the tables, in conjunction with Tensor Surface Harmonic Theory, can predict anomalous electron counts of borane clusters.

2. Group theoretical background

Consider a molecule belonging to a point group G and consisting of various fragments. Often these fragments are atoms, but in particular applications they may be ligand molecules or functional groups. The total set of fragments can be resolved into subsets (or *orbits* of the group G) containing *equivalent* units that are permuted by symmetry operations of the group. Thus the nuclear framework of a methane molecule falls into two orbits

$$CH_4 = [C] + [H^{[1]} \ldots H^{[4]}]$$
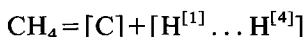
but for $B_6H_6^{2-}$ it may be convenient to treat the molecule either as a sum of atoms or of $-BH$ units

$$B_6H_6 = [(BH)^{[1]} \ldots (BH)^{[6]}].$$
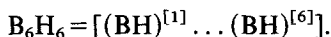
Each orbit O_A is characterised by a *site symmetry* group, H_A, a subgroup of G which describes the symmetry of the world as seen from one atom in the orbit. Consideration of those elements of symmetry which may pass through an atom not situated at the centre of a molecule [9] shows that for a non-central atom H_A must be one of C_1, C_s, C_n or C_{nv} ($n \geq 2$). If there is an atom at the centre, it has the full molecular symmetry G. The order of the orbit O_A, i.e. the number of equivalent fragments in the set, is the ratio of the orders of G and H_A. The largest orbit of G is generated by the action of the symmetry operations on a point in the general position; the order of this orbit is $|G|$ and its site symmetry group is C_1. As an illustration of these concepts, Fig. 1 shows all the orbits of the D_{4h} point group.

For any orbit of non-central fragments we may define a spherical surface passing through all the members of the set. Functions associated with each fragment may then be classified as σ, π, $\delta \ldots$ with respect to the radial vector from the centre of the sphere. The reducible representation of G generated by a σ function on each member of an orbit is Γ_σ, the permutation representation. Its character under any operation of G is simply the number of points in the orbit left unshifted by that operation. Similarly Γ_π (Γ_δ) are the representations generated by a *pair* of π (δ) functions on each fragment.

Some other representations to be defined are Γ_0, Γ_ε, Γ_{XYZ} and Γ_{REG}. Γ_0 is the *totally symmetric* representation with character +1 under every operation. Γ_ε is the *antisymmetric* or pseudoscalar representation with character +1 under proper and −1 under improper operations. Γ_{XYZ} is the representation of a set of cartesian unit vectors at the origin. Γ_{REG} is the *regular* representation, the reducible representation in which each irreducible representation of G appears a number
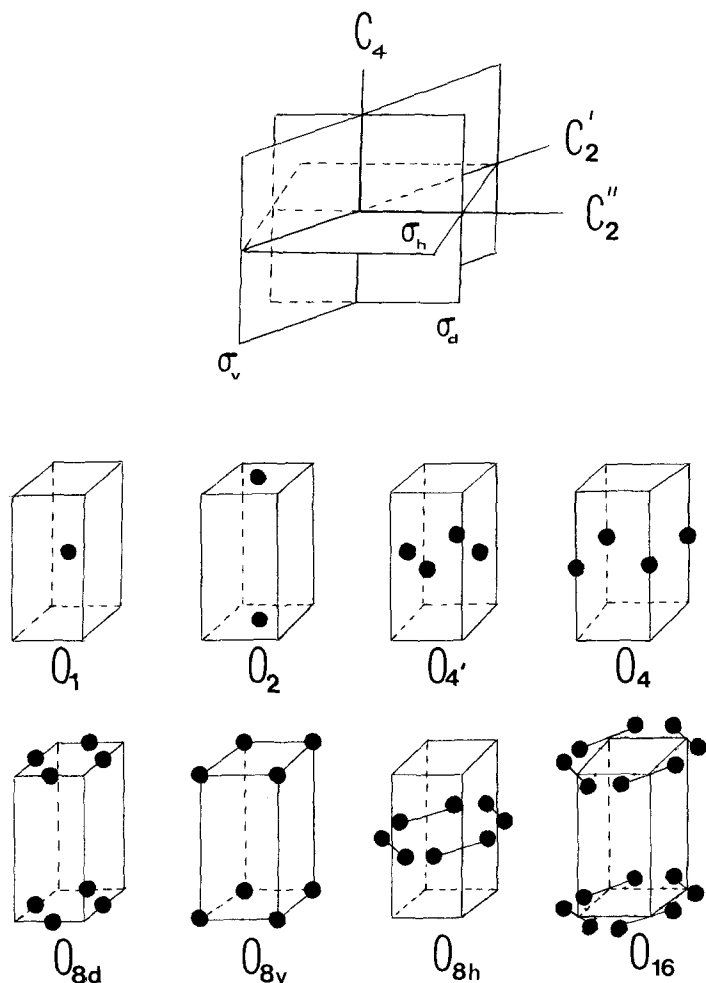
Fig. 1. Orbits of the D_{4h} point group. The first diagram shows the orientation of the symmetry elements, and the others show the eight distinct orbits of the group. O_1 is a single point lying on all symmetry elements. O_2 is a pair of points lying on C_4, related by the horizontal mirror plane. $O_{4'}$ and O_4 are sets of four points in σ_h lying on C_2'' or C_2' axes respectively. O_{8d} and O_{8v} are sets of eight points in the σ_d or σ_v vertical planes but not in σ_h. O_{8h} is a set of eight points in σ_h but not on any rotational axis. O_{16} is the set of 16 points produced by each of the 16 operations of the group acting on a point in the general position. These orbits and their site groups are listed in Table 1

of times equal to its dimension. Thus each one-dimensional representation occurs once, each doubly-degenerate representation twice and so on. Separably degenerate representations (such as E in C_3) *appear only once.* The character of Γ_{REG} is $|G|$ under the identity but zero under all other operations. Thus Γ_{REG} is the σ representation of the largest orbit of G.

As stated above, the character of Γ_σ is easily derived for any orbit. A very convenient method for the derivation of π, δ and higher representations is given

in [8]. For Γ_π and Γ_δ we have

$$\Gamma_\pi = \Gamma_\sigma \times \Gamma_{XYZ} - \Gamma_\sigma \tag{1}$$

$$\Gamma_\delta = \Gamma_\pi \times \Gamma_{XYZ} - \Gamma_\pi - \Gamma_\sigma \times (\Gamma_0 + \Gamma_\varepsilon) \tag{2}$$

and for higher angular momentum functions $(L \geq 2)$

$$\Gamma_{L+1} = \Gamma_L \times \Gamma_{XYZ} - \Gamma_L - \Gamma_{L-1} \tag{3}$$

Γ_L for a molecule can be obtained by summing over for all the orbits present in the structure. Thus from a tabulation of Γ_σ, Γ_π ... for all the orbits of a particular point group, the representations for any molecule of that symmetry may be written down by inspection. This is a similar approach to the Brester tables for symmetries of normal modes [9, 10] but gives more information, allowing us for instance to pick out the symmetries of the CO stretches in a carbonyl complex by inspection (Sect. 4). Tables of σ, π, δ ... representations are also applicable to problems in MO theory and the split into σ and π symmetries assumes particular significance in the theory of bonding in clusters (Sect. 5).

Finally, it should be mentioned that the σ, π ... representations can also be treated in terms of "ascent in symmetry" [9, 11]. Suppose that a function is a basis for a representation Γ_f in the site symmetry group of the fragment (H_A). The assembly of such functions spans a representation Γ_F in the molecular point group (G) where Γ_F may be determined by following Γ_f through the ascent in symmetry from H_A to G. In these terms, Γ_σ arises from the totally symmetric representation Γ_0 in H_A whereas Γ_π comes from the remainder of the vector representation $\Gamma_{XYZ} - \Gamma_0$. (In the allowed site groups Γ_{XYZ} always contains Γ_0.) Γ_σ, Γ_π ... could be derived by using the ascent-in-symmetry tables [11] though the present method is perhaps more straightforward.

3. The tables

To construct a set of tables which will be useful for *all* molecules of a given point group it is only necessary to obtain Γ_σ, Γ_π, Γ_δ for each possible orbit of the group. It is a straightforward task to enumerate the orbits of any given group and this has been done for most of the useful point groups by Brester [10], Jahn and Teller [12]. The corresponding site groups are listed by Rytter [13].

For any orbit, the σ representation is obtained by inspecting the effect of symmetry orbitals on the set of points in the orbit. Γ_π and Γ_δ can then be found using (1) and (2). It is convenient to carry out this step with the character form of Γ_σ and then reduce the results in the usual way.

Table 1 lists Γ_σ, Γ_π and Γ_δ for all the orbits of the common molecular point groups. In the table some conventions are used, and these are as follows. O_n denotes an orbit of order n. The column labelled "m" gives a symbol for the number of times the orbit occurs in a particular molecule, following the notation used in [10]. Thus m_0 is the number of sets of nuclei on all elements of symmetry; m_2, m_3, m_4, ... m_v, m_d, m_h, m_2, m_{2x}, ... m_{yz} are numbers of sets associated with

Table 1. σ, π and δ representations of molecular point groups, broken down by orbit. O_n is the orbit of order n and m is the number of times it occurs in a particular molecule. Further explanation of the symbols is given in the text. For each group the regular representation is given explicitly as the σ representation for the largest orbit, but otherwise abbreviated as Γ_{REG}. * Denotes a central O_1 orbit

Point group	Orbit	Site group	m	Γ_σ	Γ_π	Γ_δ
C_1	O_1	C_1	m	A	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_s^*	O_2	C_1	m	$A'+A''$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_i^*	O_2	C_1	m	A_g+A_u	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_2	O_1	C_2	m_0	A	2B	2A
	O_2	C_1	m	$A+B$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_3	O_1	C_3	m_0	A	E	E
	O_3	C_1	m	$A+E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_4	O_1	C_4	m_0	A	E	2B
	O_4	C_1	m	$A+B+E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_5	O_1	C_5	m_0	A	E_1	E_2
	O_5	C_1	m	$A+E_1+E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_6	O_1	C_6	m_0	A	E_1	E_2
	O_6	C_1	m	$A+B+E_1+E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_2^*	O_{2x}	C_2	m_{2x}	$A+B_3$	$2B_1+2B_2$	$2\Gamma_\sigma$
	O_{2y}	C_2	m_{2y}	$A+B_2$	$2B_1+2B_3$	$2\Gamma_\sigma$
	O_{2z}	C_2	m_{2z}	$A+B_1$	$2B_2+2B_3$	$2\Gamma_\sigma$
	O_4	C_1	m	$A+B_1+B_2+B_3$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_3^*	O_2	C_3	m_3	A_1+A_2	2E	2E
	O_3	C_2	m_2	A_1+E	$2A_2+2E$	$2\Gamma_\sigma$
	O_6	C_1	m	A_1+A_2+2E	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_4^*	O_2	C_4	m_4	A_1+A_2	2E	$2B_1+2B_2$
	$O_{4'}$	C_2	$m_{2'}$	A_1+B_2+E	$2A_2+2B_1+2E$	$2\Gamma_\sigma$
	O_4	C_2	m_2	A_1+B_1+E	$2A_2+2B_2+2E$	$2\Gamma_\sigma$
	O_8	C_1	m	$A_1+A_2+B_1+B_2+2E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_5^*	O_2	C_5	m_5	A_1+A_2	$2E_1$	$2E_2$
	O_5	C_2	m_2	$A_1+E_1+E_2$	$2A_2+2E_1+2E_2$	$2\Gamma_\sigma$
	O_{10}	C_1	m	$A_1+A_2+2E_1+2E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_6^*	O_2	C_6	m_6	A_1+A_2	$2E_1$	$2E_2$
	$O_{6'}$	C_2	$m_{2'}$	$A_1+B_2+E_1+E_2$	$2A_2+2B_1+2E_1+2E_2$	$2\Gamma_\sigma$
	O_6	C_2	m_2	$A_1+B_1+E_1+E_2$	$2A_2+2B_2+2E_1+2E_2$	$2\Gamma_\sigma$
	O_{12}	C_1	m	$A_1+A_2+B_1+B_2+2E_1$ $+2E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{2v}	O_1	C_{2v}	m_0	A_1	B_1+B_2	A_1+A_2
	O_{2xz}	C_s	m_{xz}	A_1+B_1	Γ_{REG}	Γ_{REG}
	O_{2yz}	C_s	m_{yz}	A_1+B_2	Γ_{REG}	Γ_{REG}
	O_4	C_1	m	$A_1+A_2+B_1+B_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{3v}	O_1	C_{3v}	m_0	A_1	E	E
	O_3	C_s	m_v	A_1+E	Γ_{REG}	Γ_{REG}
	O_6	C_1	m	A_1+A_2+2E	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{4v}	O_1	C_{4v}	m_0	A_1	E	B_1+B_2
	O_{4d}	C_s	m_d	A_1+B_2+E	Γ_{REG}	Γ_{REG}
	O_{4v}	C_s	m_v	A_1+B_1+E	Γ_{REG}	Γ_{REG}
	O_8	C_1	m	$A_1+A_2+B_1+B_2+2E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{5v}	O_1	C_{5v}	m_0	A_1	E_1	E_2
	O_5	C_s	m_v	$A_1+E_1+E_2$	Γ_{REG}	Γ_{REG}
	O_{10}	C_1	m	$A_1+A_2+2E_1+2E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{6v}	O_1	C_{6v}	m_0	A_1	E_1	E_2
	O_{6d}	C_s	m_d	$A_1+B_2+E_1+E_2$	Γ_{REG}	Γ_{REG}

Table 1 (continued)

Point group	Orbit	Site group	m	Γ_σ	Γ_π	Γ_δ
	O_{6v}	C_s	m_v	$A_1 + B_1 + E_1 + E_2$	Γ_{REG}	Γ_{REG}
	O_{12}	C_1	m	$A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{2h}^*	O_2	C_2	m_2	$A_g + A_u$	$2B_g + 2B_u$	$2\Gamma_\sigma$
	O_{2h}	C_s	m_h	$A_g + B_u$	Γ_{REG}	Γ_{REG}
	O_4	C_1	m	$A_g + A_u + B_g + B_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{3h}^*	O_2	C_3	m_3	$A' + A''$	$E' + E''$	$E' + E''$
	O_3	C_s	m_h	$A' + E'$	Γ_{REG}	Γ_{REG}
	O_6	C_1	m	$A' + A'' + E' + E''$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{4h}^*	O_2	C_4	m_4	$A_g + A_u$	$E_g + E_u$	$2B_g + 2B_u$
	O_4	C_s	m_h	$A_g + B_g + E_u$	Γ_{REG}	Γ_{REG}
	O_8	C_1	m	$A_g + A_u + B_g + B_u + E_g + E_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{5h}^*	O_2	C_5	m_5	$A' + A''$	$E_1' + E_1''$	$E_2' + E_2''$
	O_5	C_s	m_h	$A' + E_1' + E_2'$	Γ_{REG}	Γ_{REG}
	O_{10}	C_1	m	$A' + A'' + E_1' + E_1'' + E_2' + E_2''$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
C_{6h}^*	O_2	C_6	m_6	$A_g + A_u$	$E_{1g} + E_{1u}$	$E_{2g} + E_{2u}$
	O_6	C_s	m_h	$A_g + B_u + E_{2g} + E_{1u}$	Γ_{REG}	Γ_{REG}
	O_{12}	C_1	m	$A_g + A_u + B_g + B_u + E_{1g} + E_{1u} + E_{2g} + E_{2u}$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{2h}^*	O_{2z}	C_{2v}	m_{2z}	$A_g + B_{1u}$	$B_{2g} + B_{2u} + B_{3g} + B_{3u}$	$A_g + A_u + B_{1g} + B_{1u}$
	O_{2y}	C_{2v}	m_{2y}	$A_g + B_{2u}$	$B_{1g} + B_{1u} + B_{3g} + B_{3u}$	$A_g + A_u + B_{2g} + B_{2u}$
	O_{2x}	C_{2v}	m_{2x}	$A_g + B_{3u}$	$B_{1g} + B_{1u} + B_{2g} + B_{2u}$	$A_g + A_u + B_{3g} + B_{3u}$
	O_{4yz}	C_s	m_{yz}	$A_g + B_{3g} + B_{1u} + B_{2u}$	Γ_{REG}	Γ_{REG}
	O_{4xz}	C_s	m_{xz}	$A_g + B_{2g} + B_{1u} + B_{3u}$	Γ_{REG}	Γ_{REG}
	O_{4xy}	C_s	m_{xy}	$A_g + B_{1g} + B_{2u} + B_{3u}$	Γ_{REG}	Γ_{REG}
	O_8	C_1	m	$A_g + A_u + B_{1g} + B_{1u} + B_{2g} + B_{2u} + B_{3g} + B_{3u}$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{3h}^*	O_2	C_{3v}	m_3	$A_1' + A_2''$	$E' + E''$	$E' + E''$
	O_3	C_{2v}	m_2	$A_1' + E'$	$A_2' + A_2'' + E' + E''$	$A_1' + A_1'' + E' + E''$
	O_{6h}	C_s	m_h	$A_1' + A_2' + 2E'$	Γ_{REG}	Γ_{REG}
	O_{6v}	C_s	m_v	$A_1' + A_2'' + E' + E''$	Γ_{REG}	Γ_{REG}
	O_{12}	C_1	m	$A_1' + A_1'' + A_2' + A_2'' + 2E' + 2E''$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{4h}^*	O_2	C_{4v}	m_4	$A_{1g} + A_{2u}$	$E_g + E_u$	$B_{1g} + B_{1u} + B_{2g} + B_{2u}$
	$O_{4'}$	C_{2v}	$m_{2'}$	$A_{1g} + B_{2g} + E_u$	$A_{2g} + A_{2u} + B_{1g} + B_{1u} + E_g + E_u$	$A_{1g} + A_{1u} + B_{2g} + B_{2u} + E_g + E_u$
	O_4	C_{2v}	m_2	$A_{1g} + B_{1g} + E_u$	$A_{2g} + A_{2u} + B_{2g} + B_{2u} + E_g + E_u$	$A_{1g} + A_{1u} + B_{1g} + B_{1u} + E_g + E_u$
	O_{8h}	C_s	m_h	$A_{1g} + A_{2g} + B_{1g} + B_{2g} + 2E_u$	Γ_{REG}	Γ_{REG}
	O_{8d}	C_s	m_d	$A_{1g} + A_{2u} + B_{1u} + B_{2g} + E_g + E_u$	Γ_{REG}	Γ_{REG}
	O_{8v}	C_s	m_v	$A_{1g} + A_{2u} + B_{ag} + B_{2u} + E_g + E_u$	Γ_{REG}	Γ_{REG}
	O_{16}	C_1	m	$A_{1g} + A_{1u} + A_{2g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + B_{2u} + 2E_g + 2E_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$

Table 1 (continued)

Point group	Orbit	Site group	m	Γ_σ	Γ_π	Γ_δ
D_{5h}^*	O_2	C_{5v}	m_5	$A_1'+A_2''$	$E_1'+E_1''$	$E_2'+E_2''$
	O_5	C_{2v}	m_2	$A_1'+E_1'+E_2'$	$A_2'+E_2''+E_1'+E_1''+E_2'+E_2''$	$A_1'+A_1''+E_1'+E_1''+E_2'+E_2''$
	O_{10h}	C_s	m_h	$A_1'+A_2'+2E_1'+2E_2'$	Γ_{REG}	Γ_{REG}
	O_{10v}	C_s	m_v	$A_1'+A_2''+E_1'+E_1''+E_2'+E_2''$	Γ_{REG}	Γ_{REG}
	O_{20}	C_1	m	$A_1'+A_1''+A_2'+A_2''+2E_1'+2E_1''+2E_2'+2E_2''$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{6h}^*	O_2	C_{6v}	m_6	$A_{1g}+A_{2u}$	$E_{1g}+E_{1u}$	$E_{2g}+E_{2u}$
	$O_{6'}$	C_{2v}	$m_{2'}$	$A_{1g}+B_{2u}+E_{1u}+E_{2g}$	$A_{2g}+A_{2u}+B_{1g}+B_{1u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	$A_{1g}+A_{1u}+B_{2g}+B_{2u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$
	O_6	C_{2v}	m_2	$A_{1g}+B_{1u}+E_{1u}+E_{2g}$	$A_{2g}+A_{2u}+B_{2g}+B_{2u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	$A_{1g}+A_{1u}+B_{1g}+B_{1u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$
	O_{12h}	C_s	m_h	$A_{1g}+A_{2g}+B_{1u}+B_{2u}+2E_{1u}+2E_{2g}$	Γ_{REG}	Γ_{REG}
	O_{12d}	C_s	m_d	$A_{1g}+A_{2u}+B_{1g}+B_{2u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	Γ_{REG}	Γ_{REG}
	O_{12v}	C_s	m_v	$A_{1g}+A_{2u}+B_{1u}+B_{2g}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	Γ_{REG}	Γ_{REG}
	O_{24}	C_1	m	$A_{1g}+A_{1u}+A_{2g}+A_{2u}+B_{1g}+B_{1u}+B_{2g}+B_{2u}+2E_{1g}+2E_{1u}+2E_{2g}+2E_{2u}$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{2d}^*	O_2	C_{2v}	m_4	A_1+B_2	$2E$	$A_1+A_2+B_1+B_2$
	O_4	C_2	m_2	A_1+B_1+E	$2A_2+2B_2+2E$	$2\Gamma_\sigma$
	O_{4d}	C_s	m_d	A_1+B_2+E	Γ_{REG}	Γ_{REG}
	O_8	C_1	m	$A_1+A_2+B_1+B_2+2E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{3d}^*	O_2	C_{3v}	m_6	$A_{1g}+A_{2u}$	E_g+E_u	E_g+E_u
	O_6	C_2	m_2	$A_{1g}+A_{1u}+E_g+E_u$	$2A_{2g}+2A_{2u}+2E_g+2E_u$	$2\Gamma_\sigma$
	O_{6d}	C_s	m_d	$A_{1g}+A_{2u}+E_g+E_u$	Γ_{REG}	Γ_{REG}
	O_{12}	C_1	m	$A_{1g}+A_{1u}+A_{2g}+A_{2u}+2E_g+2E_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{4d}^*	O_2	C_{4v}	m_8	A_1+B_2	E_1+E_3	$2E_2$
	O_8	C_2	m_2	$A_1+B_1+E_1+E_2+E_3$	$2A_2+2B_2+2E_1+2E_2+2E_3$	$2\Gamma_\sigma$
	O_{8d}	C_s	m_d	$A_1+B_2+E_1+E_2+E_3$	Γ_{REG}	Γ_{REG}
	O_{16}	C_1	m	$A_1+A_2+B_1+B_2+2E_1+2E_2+2E_3$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
D_{5d}^*	O_2	C_{5v}	m_{10}	$A_{1g}+A_{2u}$	$E_{1g}+E_{1u}$	$E_{2g}+E_{2u}$
	O_{10}	C_2	m_2	$A_{1g}+A_{1u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	$2A_{2g}+2A_{2u}+2E_{1g}+2E_{1u}+2E_{2g}+2E_{2u}$	$2\Gamma_\sigma$
	O_{10d}	C_s	m_d	$A_{1g}+A_{2u}+E_{1g}+E_{1u}+E_{2g}+E_{2u}$	Γ_{REG}	Γ_{REG}
	O_{20}	C_1	m	$A_{1g}+A_{1u}+A_{2g}+A_{2u}+2E_{1g}+2E_{1u}+2E_{2g}+2E_{2u}$	$2\Gamma_{REG}$	$2\Gamma_{REG}$

Table 1 (continued)

Point group	Orbit	Site group	m	Γ_σ	Γ_π	Γ_δ
D_{6d}^*	O_2	C_{6v}	m_{12}	$A_1 + B_2$	$E_1 + E_5$	$E_2 + E_4$
	O_{12}	C_2	m_2	$A_1 + B_1 + E_1 + E_2 + E_3$ $+ E_4 + E_5$	$2A_2 + 2B_2 + 2E_1 + 2E_2$ $+ 2E_3 + 2E_4 + 2E_5$	$2\Gamma_\sigma$
	O_{12d}	C_s	m_d	$A_1 + B_2 + E_1 + E_2 + E_3$ $+ E_4 + E_5$	Γ_{REG}	Γ_{REG}
	O_{24}	C_1	m	$A_1 + A_2 + B_1 + B_2 + 2E_1$ $+ 2E_2 + 2E_3 + 2E_4$ $+ 2E_5$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
S_4^*	O_2	C_2	m_2	$A + B$	$2E$	$2\Gamma_\sigma$
	O_4	C_1	m	$A + B + E$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
S_6^*	O_2	C_3	m_3	$A_g + A_u$	$E_g + E_u$	$E_g + E_u$
	O_6	C_1	m	$A_g + A_u + E_g + E_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
T^*	O_4	C_3	m_3	$A + T$	$E + 2T$	Γ_π
	O_6	C_2	m_2	$A + E + T$	$4T$	$2\Gamma_\sigma$
	O_{12}	C_1	m	$A + E + 3T$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
T_d^*	O_4	C_{3v}	m_3	$A_1 + T_2$	$E + T_1 + T_2$	Γ_π
	O_6	C_{2v}	m_2	$A_1 + E + T_2$	$2T_1 + 2T_2$	$A_1 + A_2 + 2E + T_1 + T_2$
	O_{12}	C_s	m_d	$A_1 + E + T_1 + 2T_2$	Γ_{REG}	Γ_{REG}
	O_{24}	C_1	m	$A_1 + A_2 + 2E + 3T_1$ $+ 3T_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
T_h^*	O_6	C_{2v}	m_2	$A_g + E_g + T_u$	$2T_g + 2T_u$	$A_g + A_u + E_g + E_u + T_g$ $+ T_u$
	O_8	C_3	m_3	$A_g + A_u + T_g + T_u$	$E_g + E_u + 2T_g + 2T_u$	Γ_π
	O_{12}	C_s	m_h	$A_g + E_g + T_g + 2T_u$	Γ_{REG}	Γ_{REG}
	O_{24}	C_1	m	$A_g + A_u + E_g + E_u + 3T_g$ $+ 3T_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
O^*	O_6	C_4	m_4	$A_1 + E + T_1$	$2T_1 + 2T_2$	$2A_2 + 2E + 2T_2$
	O_8	C_3	m_3	$A_1 + A_2 + T_1 + T_2$	$2E + 2T_1 + 2T_2$	Γ_π
	O_{12}	C_2	m_2	$A_1 + E + T_1 + 2T_2$	$2A_2 + 2E + 4T_1 + 2T_2$	$2\Gamma_\sigma$
	O_{24}	C_1	m	$A_1 + A_2 + 2E + 3T_1$ $+ 3T_2$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
O_h^*	O_6	C_{4v}	m_4	$A_{1g} + E_g + T_{1u}$	$T_{1g} + T_{1u} + T_{2g} + T_{2u}$	$A_{2g} + A_{2u} + E_g + E_u + T_{2g}$ $+ T_{2u}$
	O_8	C_{3v}	m_3	$A_{1g} + A_{2u} + T_{2g} + T_{1u}$	$E_g + E_u + T_{1g} + T_{1u} + T_{2g}$ $+ T_{2u}$	Γ_π
	O_{12}	C_{2v}	m_2	$A_{1g} + E_g + T_{1u} + T_{2g}$ $+ T_{2u}$	$A_{2g} + A_{2u} + E_g + E_u$ $+ 2T_{1g} + 2T_{1u} + T_{2g}$ $+ T_{2u}$	$A_{1g} + A_{1u} + E_g + E_u + T_{1g}$ $+ T_{1u} + 2T_{2g} + 2T_{2u}$
	O_{24d}	C_s	m_d	$A_{1g} + A_{2u} + E_g + E_u + T_{1g}$ $+ 2T_{1u} + 2T_{2g} + T_{2u}$	Γ_{REG}	Γ_{REG}
	O_{24h}	C_s	m_h	$A_{1g} + A_{2g} + 2E_g + T_{1g}$ $+ 2T_{1u} + T_{2g} + 2T_{2u}$	Γ_{REG}	Γ_{REG}
	O_{48}	C_1	m	$A_{1g} + A_{1u} + A_{2g} + A_{2u}$ $+ 2E_g + 2E_u + 3T_{1g}$ $+ 3T_{1u} + 3T_{2g} + 3T_{2u}$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
I^*	O_{12}	C_5	m_5	$A + T_1 + T_2 + H$	$2T_1 + 2G + 2H$	$2T_2 + 2G + 2H$
	O_{20}	C_3	m_3	$A + T_1 + T_2 + 2G + H$	$2T_1 + 2T_2 + 2G + 4H$	Γ_π
	O_{30}	C_2	m_2	$A + T_1 + T_2 + 2G + 3H$	$4T_1 + 4T_2 + 4G + 4H$	$2\Gamma_\sigma$
	O_{60}	C_1	m	$A + 3T_1 + 3T_2 + 4G + 5H$	$2\Gamma_{REG}$	$2\Gamma_{REG}$

Table 1 (continued)

Point group	Orbit	Site group	m	Γ_σ	Γ_π	Γ_δ
I_h^*	O_{12}	C_{5v}	m_5	$A_g+T_{1u}+T_{2u}+H_g$	$T_{1g}+T_{1u}+G_g+G_u$ $+H_g+H_u$	$T_{2g}+T_{2u}+G_g+G_u$ $+H_g+H_u$
	O_{20}	C_{3v}	m_3	$A_g+T_{1u}+T_{2u}+G_g$ $+G_u+H_g$	$T_{1g}+T_{1u}+T_{2g}+T_{2u}$ $+G_g+G_u+2H_g$ $+2H_u$	Γ_π
	O_{30}	C_{2v}	m_2	$A_g+T_{1u}+T_{2u}+G_g$ $+G_u+2H_g+H_u$	$2T_{1g}+2T_{1u}+2T_{2g}$ $+2T_{2u}+2G_g+2G_u$ $+2H_g+2H_u$	$A_g+A_u+T_{1g}+T_{1u}$ $+T_{2g}+T_{2u}+2G_g$ $+2G_u+3H_g+3H_u$
	O_{60}	C_s	m_d	$A_g+T_{1g}+2T_{1u}+T_{2g}$ $+2T_{2u}+2G_g+2G_u$ $+3H_g+2H_u$	Γ_{REG}	Γ_{REG}
	O_{120}	C_1	m	$A_g+A_u+3T_{1g}+3T_{1u}$ $+3T_{2g}+3T_{2u}+4G_g$ $+4G_u+5H_g+5H_u$	$2\Gamma_{REG}$	$2\Gamma_{REG}$
$C_{\infty v}$	O_1	$C_{\infty v}$	m_∞	Σ^+	Π	Δ
$D_{\infty h}^*$	O_2	$C_{\infty v}$	m_∞	$\Sigma_g^+ + \Sigma_u^+$	$\Pi_g+\Pi_u$	$\Delta_g+\Delta_u$

symmetry elements $C_2, C_3, C_4 \ldots \sigma_v, \sigma_d, \sigma_h, C_2', C_{2x}, \ldots \sigma_{yz}$. m with no subscript is the number of sets of nuclei in general position, i.e. on no element of symmetry. For groups where a single atom can occupy the central position (the "point" of the point group) the $\sigma, \pi \ldots$ classification does not apply to the orbit O_1. Such groups are marked * in the table and this orbit is not listed for them. N, the total number of atoms in a molecule, is recovered by multiplying each "m" symbol by the order of the orbit. Thus for an O_h molecule

$$N = m_0 + 6m_4 + 8m_3 + 12m_2 + 24m_d + 24m_h + 48m$$

SF_6 has $m_0 = 1$ and $m_4 = 1$ whereas C_8H_8 (cubane) has $m_3 = 2$. The total σ or π representation is correspondingly derived by multiplying each "m" symbol by Γ_σ or Γ_π for the orbit. Thus for a T_d molecule

$$\Gamma_\sigma = (m_d + m_2 + m_3 + m)A_1 + mA_2 + (m_2 + m_d + 2m)E$$

$$+ (m_d + 3m)T_1 + (m_3 + m_2 + 2m_d + 3m)T_2$$

so that Γ_σ is $A_1 + T_2$ for CH_4 and $2A_1 + 2T_2$ for B_4Cl_4. Similarly Γ_π is $E + T_1 + T_2$ for CH_4.

From inspection of the table a number of mathematical properties of the σ, π, $\delta \ldots$ representations are evident. Some of these are now discussed.

(i) One obvious property of Γ_σ for any orbit is that it contains Γ_0, the totally symmetric representation, exactly once. We can always construct one totally symmetric combination by taking in-phase σ orbitals on all fragments. Since any two members of the set are exchanged by some symmetry operation, no other combination of phases can be totally symmetric. The number of times that Γ_0

occurs in the σ representation for a molecule is thus equal to the number of sets of equivalent nuclei, excluding any central atom.

(ii) The largest orbit O_G has σ representation Γ_{REG}, since the σ characters are $(|G|, 0, 0 \ldots)$. In the table it is seen that Γ_π and Γ_δ for this orbit are both $2\Gamma_{REG}$. This follows from (1) and (2). For example Γ_π is calculated from

$$
\begin{array}{llll}
\Gamma_\sigma & |G| & 0 & 0 \ldots \\
\Gamma_{XYZ} & 3 & . & . \ldots \\
\hline
(\Gamma_\sigma \times \Gamma_{XYZ}) & 3|G| & 0 & 0 \ldots \\
-\Gamma_\sigma & -|G| & 0 & 0 \ldots \\
\hline
\Gamma_\pi & 2|G| & 0 & 0 \ldots
\end{array}
$$

The recursion relation (3) may be used in a similar way to show that

$$\Gamma_\pi = \Gamma_\delta = \Gamma_L(L > 2) = 2\Gamma_\sigma = 2\Gamma_{REG} \quad \text{for } O_G$$

(iii) Many of the point groups in the table have an orbit of order $\frac{1}{2}|G|$. The site group of such an orbit must be C_2 or C_s, and in each case regularities in the higher Γ_L arise. When the site group is C_s it may be shown by considering characters that both Γ_π and Γ_δ are equal to Γ_{REG}. It is not difficult to prove that this holds for all higher L and thus

$$\Gamma_L(L > 0) = \Gamma_{REG} \quad \text{(for half orbit with } H_A = C_s)$$

When the site group is C_2 it is seen from the table that $\Gamma_\delta = 2\Gamma_\sigma$. Again using arguments based on characters it is easily proved that the general pattern is an alternating series with, for even angular momentum,

$$\Gamma_{2L}(L > 0) = 2\Gamma_\sigma \quad \text{(for half orbit with } H_A = C_2)$$

and for odd angular momentum

$$\Gamma_{2L+1}(L > 0) = \Gamma_\pi \quad \text{(for half orbit with } H_A = C_2)$$

(iv) Another regularity that emerges on inspection of the table is that for site groups C_3 and C_{3v} the δ representation is equal to Γ_π. It can be shown that this is part of a more general pattern which depends on $L(\mathrm{mod}\,3)$. Thus for $H_A = C_3$

$$L = 0, 1, 2, 3, 4, 5, 6, \ldots$$

$$\Gamma_L = \Gamma_\sigma, \Gamma_\pi, \Gamma_\pi, 2\Gamma_\sigma, \Gamma_\pi, \Gamma_\pi, 2\Gamma_\sigma, \ldots$$

and for $H_A = C_{3v}$

$$\Gamma_L = \Gamma_\sigma, \Gamma_\pi, \Gamma_\pi, \Gamma_\sigma \times (\Gamma_0 + \Gamma_\varepsilon), \Gamma_\pi, \Gamma_\pi, \Gamma_\sigma \times (\Gamma_0 + \Gamma_\varepsilon) \ldots$$

The repeat length of 3 in this pattern is associated with the C_3 axis in the site symmetry. The results in paragraph (iii) show a pattern with period 2 for the cyclic site groups of order 2. For a C_{2v} site group we have

$$\Gamma_L = \Gamma_\sigma, \Gamma_\pi, \Gamma_\sigma \times (\Gamma_0 + \Gamma_\varepsilon), \Gamma_\pi, \Gamma_\sigma \times (\Gamma_0 + \Gamma_\varepsilon), \Gamma_\pi, \ldots$$

and in general a C_n or C_{nv} site symmetry group will produce a repeating pattern in Γ_L with a period equal to the order of the principal axis. In the extreme case of $C_{\infty v}$ site symmetry in linear molecules the pattern never repeats.

(v) The axial groups C_n and C_{nv} have a single-point orbit O_1 for which the σ, π ... classification can be applied. Trivially, this orbit has site symmetry equal to the full point group and $\Gamma_\sigma = \Gamma_0$, $\Gamma_\pi = \Gamma_{XYZ} - \Gamma_0$.

(vi) Other relationships between representations for *different* orbits of the same group exist. For instance in I_h

$$\Gamma_\sigma(O_{60}) = \Gamma_\sigma(O_{20}) + \Gamma_\pi(O_{20})$$

$$\Gamma_\sigma(O_{60}) = \Gamma_\sigma(O_{12}) + \Gamma_\pi(O_{12}) + \Gamma_\delta(O_{12})$$

Both are explained by noting that two realisations of the 60-orbit of I_h are the truncated dodecahedron and the truncated icosahedron, so that the 60-vertex orbit can be constructed either from 20 triangles or 12 pentagons.

4. Applications: (i) molecular vibrations

The present tables can be used to give an orbit-by-orbit breakdown of the vibrational symmetry of a molecule, the same information as carried by the Brester tables [10]. In addition they allow an analysis of molecular vibrations into group stretches and bends to be made by inspection.

Γ_{3N} is the representation spanned by the 3N independent displacements of the N atoms in a polyatomic molecule. This is related to the symmetry of the vibrations, rotations and translations by

$$\Gamma_{3N} = \Gamma_{VIB} + \Gamma_{ROT} + \Gamma_{TRAN}$$

and to σ and π representations by

$$\Gamma_{3N} = \Gamma_\sigma + \Gamma_\pi = \Gamma_\sigma \times \Gamma_{XYZ}$$

for molecules without an atom in a unique, central position, or

$$\Gamma_{3N} = \Gamma_\sigma \times \Gamma_{XYZ} + \Gamma_{XYZ}$$

for molecules with an atom at the "point" of the point group (i.e. belonging to groups marked * in the table). The translational representation is just $\Gamma_{TRAN} = \Gamma_{XYZ}$ and (for nonlinear molecules) the rotations transform as $\Gamma_\varepsilon \times \Gamma_{XYZ}$.

We can therefore find Γ_{VIB} for a molecule by inspection of the table. For example, a C_{3v} molecule has

$$\Gamma_\sigma = (m_0 + m_v + m)A_1 + mA_2 + (m_v + 2m)E$$

and

$$\Gamma_\pi = (m_v + 2m)A_1 + (m_v + 2m)A_2 + (m_0 + 2m_v + 4m)E.$$

Since in C_{3v} $\Gamma_{XYZ} = A_1 + E$ and $\Gamma_{ROT} = A_2 + E$, the vibrational representation is

$$\Gamma_{VIB} = (m_0 + 2m_v + 3m - 1)A_1 + (m_v + 3m - 1)A_2 + (m_0 + 3m_v + 6m - 2)E$$

in agreement with [9].

On the other hand, the Brester tables cannot be applied to problems such as the determination of the symmetry of the eight CN stretching modes of $Mn(CN)_8^{4-}$. The CN bond lengths form a realisation of the O_{8d} orbit of the D_{4d} group, and their stretches are σ displacements. The symmetry of the eight stretches is therefore, from the Table,

$$\Gamma_\sigma(O_{8d}, D_{4d}) = A_1 + B_2 + E_1 + E_2 + E_3$$

See [9] for a treatment of this example by the method of ascent in symmetry.

A standard application of group theory uses the number of infrared- or Raman-active CO stretches of a carbonyl to distinguish between alternative possible geometries. Thus, from the table, CO stretches in a hypothetical trigonal-bipyramidal pentacarbonyl span

$$\Gamma_\sigma(O_2, D_{3h}) + \Gamma_\sigma(O_3, D_{3h}) = 2A_1' + A_2'' + E'(2 \text{ ir, } 3 \text{ Raman})$$

whereas a C_{4v} geometry would lead to

$$\Gamma_\sigma(O_1, C_{4v}) + \Gamma_\sigma(O_{4v}, C_{4v}) = 2A_1 + B_1 + E \text{ (3 ir, 4 Raman)}$$

5. Applications: (ii) electronic structure of clusters

The concepts of σ and π pseudosymmetries have an obvious utility in the molecular orbital theory of complexes and clusters. It is trivial for example to use Table 1 to assign point-group symmetries to the σ metal–carbonyl bonds in $Cr(CO)_6$ (Γ_σ for O_6 in O_h) and to the π^* tangential ligand orbitals available for back-donation from the metal (Γ_π for O_6 in O_h).

In this section we review one particular application, to the electron counts of *closo*-boranes $B_nH_n^{2-}$. These molecules are deltahedral in shape and held together by $(n+1)$ skeletal pairs (for $5 \leq n \leq 12$) [14]. However tetrahedral clusters with a skeleton of four main group atoms require either 4 (B_4Cl_4) or 6 (P_4) but not 5 skeletal pairs. Three members of the hypothetical supra-icosahedral series ($13 \leq n \leq 24$) are also predicted to use n or $(n+2)$ but not $(n+1)$ pairs [15, 16]. A recent group-theoretical analysis [17] of Stone's TSH (tensor surface harmonic) theory of clusters [2–5] showed that in both cases the non-Wade electron count is *forced* by the point-group symmetry of the cluster. The general criterion for a non-Wade count is found by considering Γ_π, as reviewed in the present section.

In TSH the skeletal molecular orbitals of a cluster are approximated by the solutions of a model problem – the free electron on a sphere. These analytical functions are the scalar spherical harmonics (σ), the even (π) and odd ($\bar{\pi}$) vector surface harmonics, the even (δ) and odd ($\bar{\delta}$) tensor surface harmonics, and higher functions. For the infinite, spherical model cluster there are three infinite series of MOs ($S^\sigma, P^\sigma, D^\sigma, \ldots L^\sigma; P^\pi, \ldots L^\pi; \bar{P}^\pi, \ldots \bar{L}^\pi$) but for a finite cluster we count only the first n independent functions of σ, π, and $\bar{\pi}$ type respectively. In spherical symmetry L^σ and L^π span the same representation and can interact whereas $\bar{L}^\pi$ cannot mix with either within the TSH model. In a *finite* group the σ MOs span Γ_σ, $(\pi + \bar{\pi})$ MOs span Γ_π ($\delta + \bar{\delta}$) span Γ_δ and so on. More detailed reasoning

[3] shows that for a normal deltahedral cluster the $(n+1)$ skeletal pairs occupy S^σ and the n bonding L^σ/L^π combinations, leaving all $\bar{L}^\pi$ and the antibonding L^σ/L^π combinations empty.

Although the π and $\bar{\pi}$ MOs are of different spherical symmetries they are related by a pairing principle. A π orbital is converted to a $\bar{\pi}$ orbital by the parity operation, a twist of each tangential p orbital in the cluster through 90^0, all in the same sense. Stone has shown that this implies a mirror relationship between bonding π and antibonding $\bar{\pi}$ energies [5]. This persists even after $\sigma - \pi$ mixing is taken into account [18]. Mathematical aspects of the parity transformations are discussed in detail in [19] and its effect on δ orbitals of metal halide clusters in [7, 20].

In terms of representations the parity operation transforms as Γ_ε so that

$$\Gamma(L^\pi) = \Gamma(\bar{L}^\pi) \times \Gamma_\varepsilon$$

$$\Gamma(\bar{L}^\pi) = \Gamma(L^\pi) \times \Gamma_\varepsilon$$

If we define representations as *conjugate* when they are related by the parity operation, i.e. Γ_A and Γ_B are conjugate if $\Gamma_A = \Gamma_B \times \Gamma_\varepsilon$ and $\Gamma_B = \Gamma_A \times \Gamma_\varepsilon$, then the L^π and $\bar{L}^\pi$ representations are conjugate. In the spherical group, moreover, Γ_A and Γ_B are always distinct. However for the finite groups there are three possibilities [17]:

(i) Γ_A is always distinct from its conjugate Γ_B. Groups of this type contain the inversion or a σ_h mirror plane. They include C_i, C_s, C_{2v}, $D_{(2n+1)d}$, C_{nh}, $S_{(4n-2)}$, D_{nh}, T_h, O_h and I_h.

(ii) Γ_A is always *self-conjugate*. Groups of this type describe chiral molecules and include C_n, D_n, T, O and I.

(iii) Some Γ_A are self-conjugate and some are not. The self-conjugate representations have zero character under improper operations and are doubly degenerate. Groups of this type are C_{nv} $(n > 2)$, S_{4n}, D_{2nd} and T_d.

These considerations are relevant to the theory of clusters because TSH assigns essentially bonding character to L^π and antibonding character to $\bar{L}^\pi$. In case (i) the total representation $\Gamma(\pi + \bar{\pi})$ splits into two distinct subshells [21]. In case (ii) it is, with one exception, easy to assign π and $\bar{\pi}$ just by counting half of Γ_π as π and half as $\bar{\pi}$. The exception is when there is an odd number of a self-conjugate E-type species in Γ_π. This may happen also for case (iii).

If $\Gamma_\pi = \Gamma(\pi + \bar{\pi})$ contains an odd number of a self-conjugate E symmetry species, the cluster is forced by symmetry to show a non-Wade count [19]. If one MO component of the E set is π, the other is $\bar{\pi}$ and since the two are degenerate, they must be nonbonding. If this pair of MOs is empty the cluster has n skeletal pairs, if full $(n+2)$. Intermediate occupations would lead to Jahn–Teller distortion and loss of symmetry.

Inspection of Table 1 reveals that for most symmetry groups of types (ii) and (iii) the representation Γ_π contains an *even* number of the self-conjugate E

Table 2. Occurrence of odd numbers of self-conjugate symmetry species in $\Gamma_\pi \cdot n$ is greater than 2

Group	Rep	Number
C_n	E or E_1	$m_0 + 2m$
T	E	$m_3 + 2m$
C_{nv}	E or E_1	$m_0 + 2m_v + 4m$ (n odd)
	E or E_1	$m_0 + 2m_v + 2m_d + 4m$ (n even)
T_d	E	$m_3 + 2m_d + 4m$

species. The exceptions are listed in Table 2 and from them we derive the rules stated in [17]. A C_n or C_{nv} deltahedral cluster (n > 2) has a non-Wade count if the number of skeletal atoms on the C_n axis is odd. A T or T_d cluster has a non-Wade count if the number of sets of four equivalent skeletal atoms is odd. B_4H_4 and the hypothetical [15] $B_{16}H_{16}$ and $B_{22}H_{22}$ clusters exemplify the second rule, whereas the hypothetical $B_{19}H_{19}$ cluster has C_{3v} symmetry and illustrates the first case.

In fact, as Johnston and Mingos have pointed out [21], only if n = 3 can the cluster with an odd number of atoms on the principal axis be *both* C_{nv} (or C_n) *and* deltahedral. The cases where n > 3 are *nido* clusters (which do indeed have n + 2 skeletal pairs). With this restriction the two rules simplify: a deltahedral cage of T, T_d, C_3 or C_{3v} symmetry has a non-Wade electron count whenever the number of cage atoms is 3p + 1 [21].

6. Applications: (iii) the spherical shell technique

The data in Table 1 facilitate the construction of symmetry-adapted LCAO functions and symmetry coordinates of molecular motion for any orbit on a unified basis within the spherical shell technique [6-9]. The symmetry aspects of TSH theory are exploited to give pictorial representations of symmetry-adapted functions using a cartographic device, the Mollweide projection. On any orbit the σ symmetry-adapted functions are linear combinations of the local σ components with coefficients determined by the value of the appropriate central spherical harmonic at each atomic position. Within the spherical shell technique [6-8] the orbit geometry is superimposed on Mollweide projections of these central harmonics. For an orbit of n atoms the σ symmetry-adapted functions are the first n distinct linear combinations to emerge from the superimposition process.

In qualitative molecular orbital theory the local σ components of these symmetry-adapted functions are atomic orbitals at each position in an orbit. The orbitals can be of s, p_σ, d_σ ... type, and because of the constant overlap between neighbouring components the molecular orbital energies increase with the angular momentum quantum number of the central harmonic.

For molecular motion, the σ component functions are radial displacements of

the atoms and the symmetry-adapted linear combinations contribute to the vibrational normal modes and to overall translation of the molecule.

For example, consider the construction of the σ-LCAO functions for the B_{12} cage of $B_{12}H_{12}^{2-}$. The structure has I_h symmetry and the 12σ MOs are the first 12 distinct combinations of the local components obtained by superimposition of the structure on the icosahedral harmonics [22, 23]. The results are shown in
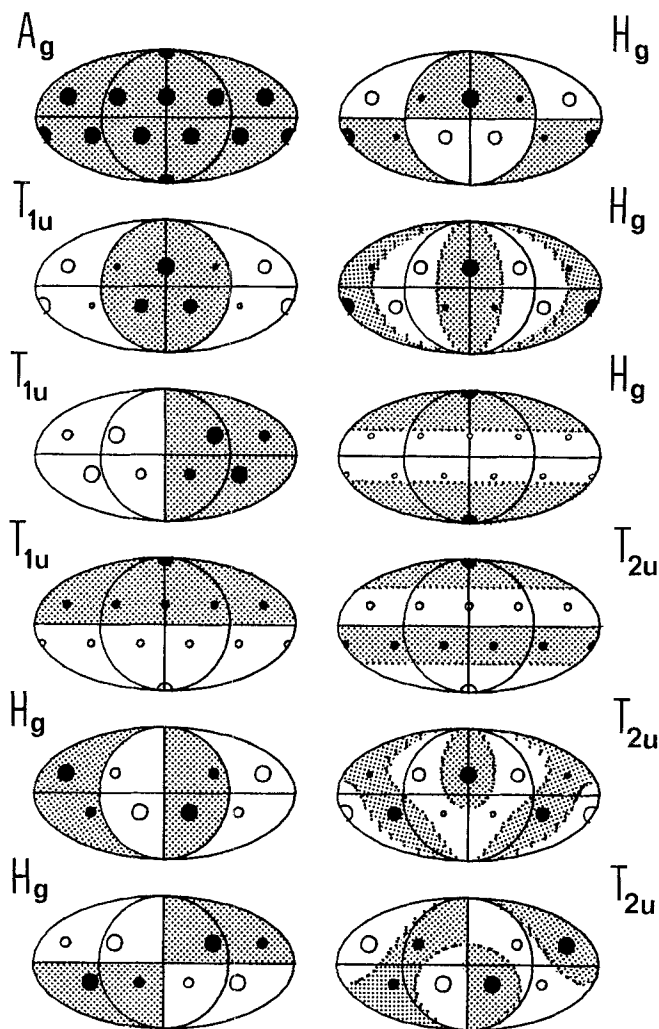

Fig. 2. Spherical shell decomposition of the σ representation generated by the B_{12} cage in I_h symmetry. The cage geometry is superimposed on Mollweide projections of the icosahedral harmonics. The *shading* represents regions where the harmonics are positive. The *filled circles* represent positive amplitude for the local component, and the *size* of the local symbol represents the magnitude of the coefficient (equal to the value of the central harmonic). *Open circles* and *unshaded* portions represent negative amplitudes. For LCAO theory the symbols represent σ-oriented atomic orbitals; for molecular motion the *filled circles* indicate radial extension and *open circles* contraction
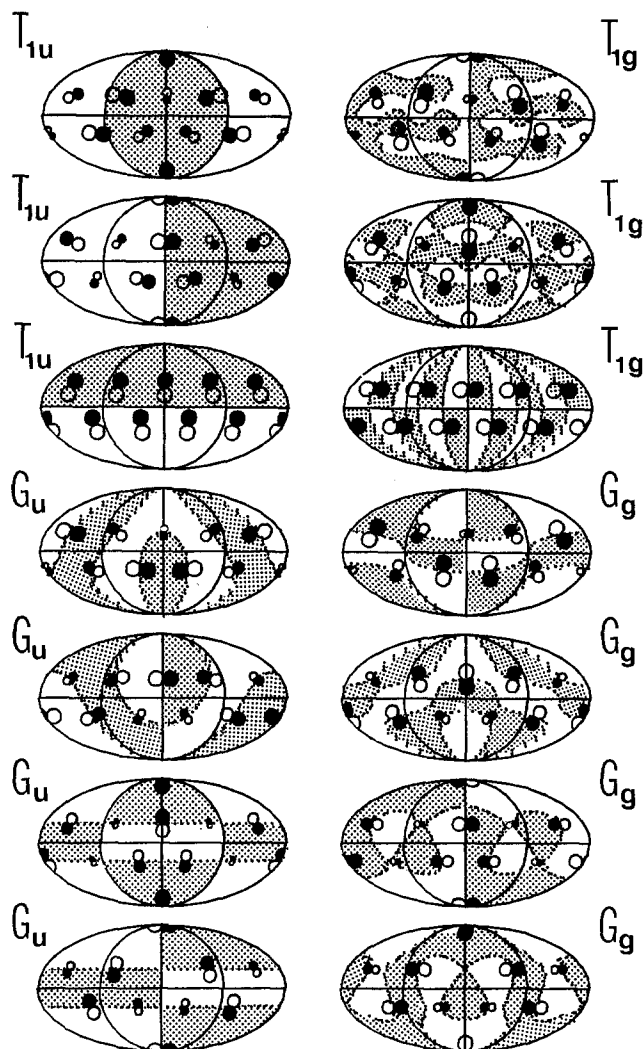
Fig. 3. Spherical shell analysis for π and $\bar{\pi}$ functions on the unit sphere. In the standard orientation π_θ components point South and π_ϕ components point East. The symmetry-adapted combinations lie in the local direction of maximum gradient of the central harmonic. As in Fig. 2, the size of the local symbol indicates the relative contribution to the global combination. Diagrams in the *left hand column* correspond in LCAO theory to π orbitals of the B_{12} cage and those on the right to $\bar{\pi}$ orbitals. Note that the sets are interchanged on local rotation of the components through 90°. In molecular vibration theory the T_{1g} set corresponds to overall rotation (taking the phase of the atomic p orbital to indicate the direction of motion on the surface). The T_{1u} sets mix vibration and rotation as discussed in the text

Fig. 2. The LCAO coefficients are readily determined from the magnitude of the appropriate harmonic at each atomic position, and the size of the local symbols is used to indicate the relative contribution to the MO.

Alternatively, considering the results as symmetry coordinates for motion of the B_{12} cage, it is clear from the figure that the T_{1o} displacements are mainly overall translation along the x, y and z directions (with the notation that ● corresponds to radial extension, and ○ to contraction). The remaining diagrams of the figure correspond to approximate normal vibrations based on radial "stretching".

The π local components describe angle-changing motions. They span T_{1u}, H_g, G_u, T_{1g}, H_u and G_g symmetries and the last three sets can be obtained from the first three by local rotation of all components through 90°.
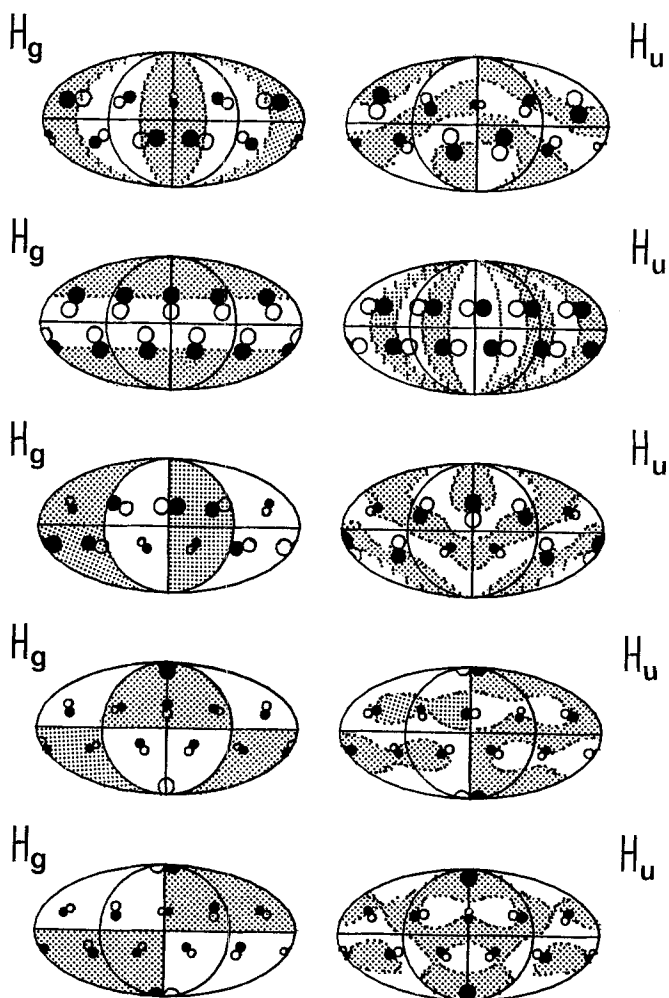

Fig. 3. continued

The spherical shell analysis is set out in Fig. 3 where it is evident that the parity transformation corresponding to local rotations through 90° does indeed interconvert g and u functions. In molecular orbital theory the diagrams of Fig. 3 are representations of the p_π-based molecular orbitals for the B_{12} cage with the LCAO coefficients given by the first partial derivatives of the icosahedral harmonics with respect to θ and ϕ [6-9] at each atomic position. To determine orbital energies, it is necessary to allow for mixing of σ and π MOs as in TSH theory [2].

For the analysis of molecular motion it is clear that the T_{1g} combinations of angular distortions correspond to molecular rotation about the x, y and z axes. The remaining combinations can be assigned as angle-changing molecular vibrations with the exception of the T_{1u} set which mix translation and vibration. The normal modes of T_{1u} symmetry can be obtained by suitable combination of the σ and π sets so that the symmetry coordinates correspond to one set of pure angle distortions and a set of pure translations. For *quantitative* treatment of the normal vibrations it is necessary to mix "radial" and "angular" coordinates of the same symmetry. In this case the H_g modes of Figs. 2 and 3 must be combined to diagonalise the force field. Mixing with the B–H stretching vibrations would also occur in the full treatment of $B_{12}H_{12}^{2-}$.

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