Commentationes

The Electronic Structure of the Boron Hydrides

Part IV. The Atomic Orbital Composition of Topological Bases

S. F. A. KETTLE* and D. J. REYNOLDS**

Department of Chemistry, The University, Sheffield S 3 7 HF, England

The expansion of topological basis functions for tetrahedral and octahedral boron cage molecules in terms of an explicit atomic orbital basis is considered. A maximum localisation criteria is used to define mixing coefficients. The overlap between 'face' basis functions in the two geometries is 0.79 and only a very crude parameter transferability exists. However, some aspects of the relative molecular orbital energy levels generated with a topological basis appear to be an improvement on those using an atomic orbital basis.

Die Entwicklung topologischer Basisfunktionen nach einer expliziten Basis von Atomorbitalen für käfigförmige, tetraedrische und oktaedrische Moleküle, die Boratome enthalten, wird untersucht. Ein Kriterium maximaler Lokalisierung wird zur Bestimmung der Mischungskoeffizienten verwendet. Die Überlappung zwischen den Basisfunktionen, die zu den Seiten der beiden Geometrien gehören, beträgt 0,79, und es existiert nur eine ungefähre Übertragbarkeit der Parameter. Einige Aspekte der relativen MO-Energiewerte, die mit einer topologischen Basis gewonnen wurden, stellen eine Verbesserung gegenüber der Verwendung einer Atomorbitalbasis dar.

Développement des fonctions de base topologiques en termes d'une base explicite d'orbitales atomiques pour des molécules cages de bore tétraédrique et octaédrique. Un critère de localisation maximum est utilisé pour définir les coéfficients de mélange. Le recouvrement entre les fonctions de base 'faciales' dans les deux géométries est de 0.79 et la transférabilité des paramètres n'est que très grossière. Cependant, certains aspects relatifs des niveaux d'énergie des orbitales moléculaires engendrées avec une base topologique apparaissent plus satisfaisants que ceux obtenus avec une base d'orbitales atomiques.

It is only relatively recently that accurate quantum mechanical calculations have been performed on the boron hydrides [1]. However, the activity in this field is such that in the near future all of the important members of the series will have been studied. When this situation is reached the necessity for a simple but yet reasonably accurate discussion of the bonding in these molecules will remain. For many years the three-centered bond concept has provided a reasonably adequate explanation of the closed-shell structure of these molecules and it seems probable that any refined theory will be based on it. We have recently attempted such a refinement in formulating a topologically-correct extension of Hückel theory to polyhedral molecules [2–4]. Although this treatment falls far

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* Present address: School of Chemical Sciences, University of East Anglia, Norwich, NOR 88 C, England.
** Present address: Fulmer Research Institute, Stoke Poges, Bucks, England.

short of the rigour of a full SCF calculation, it has been found to provide an acceptable semi-quantitative picture of the molecular orbital structure of the P_4 molecule [5]. We may reasonably hope, therefore, that the same situation will prevail for the boron hydrides. Indeed, a topological basis set may provide a convenient basis for an SCF treatment, a possibility we are currently exploring. A necessary first step in this work is to establish the relationship between a topological and atomic orbital basis and it is this problem which we discuss in the present paper. It will transpire that there is no unique relationship between the two bases notwithstanding the fact that the number of variables may be small. Although it is evident that these variables may be determined as part of an SCF refinement, in the present paper we use an alternative approach.

In previous papers of this series [2–4] we have discussed the use of either a three-centre potentially bonding orbital corresponding to a (triangular) polyhedron face or a two-centre potentially bonding orbital corresponding to a polyhedron edge, as a basis for a semi-quantitative description of the MO energy level patterns of the boron hydrides. For these two bases, within a Hückel-type formalism, one obtains patterns of molecular orbital energy levels which agree with each other and with calculations performed using an explicit atomic orbital basis set. For the case of closed polyhedral ('cage') boron hydrides the orbital energies obtained using the two topological bases are particularly simply related to each other and we have shown that this is a consequence of their topological relationship [4].

In the present paper we consider the explicit form of the topological basis sets expressed as linear combinations of atomic orbitals. The discussion we give is applicable equally to 'cage' (closed polyhedra) and 'basket' (open polyhedra) boron hydrides.

Consider an orthonormal topological basis set B. This set is related by a unitary transformation matrix U to the set of orthonormal symmetry-correct molecular orbitals M which are a solution of the secular problem

$$UB = M .$$

The members of the set M are linear combinations of a set of non-orthogonal symmetry-correct orbitals N, $M = TN$, where the transformation matrix T is not unique (vide infra). The set N may be expressed in terms of an atomic orbital basis A by an appropriate transformation matrix V

$$VA = N$$

so

$$B = U^{-1}TVA . \tag{1}$$

Given A, and the molecular geometry, the basis B is defined except for the mixing coefficients in T. These may be determined by additional, physically reasonable, constraints. For example, one might impose the condition that the members of B are as localized as possible. The composition of the edge and face bases is then determined as are also the explicit forms of the Hückel energy parameters (and, of course, matrix elements of a Hamiltonian which explicitly includes electron repulsion terms).

It is readily demonstrated group theoretically that for the valence orbital set available for the boron hydrides one cannot define orthogonal face (F) and edge (E)

bases, a point which distinguishes these molecules from clusters of transition metal atoms [6, 7]. It is physically reasonable therefore, to require that each basis leads to identical sets of molecular eigenfunctions, insofar as they map onto each other. This is equivalent to the requirement that corresponding mixing coefficients be identical in the two transformation matrices, T_F and T_E.

In view of their non-orthogonality, it is of interest to investigate the overlap between members of the edge and face bases. It is convenient to replace the non-orthogonal atomic orbital basis set A by an orthogonalised set D,

$$D = RA$$

where the transformation matrix R might be taken as $S^{-\frac{1}{2}}$, where $A \cdot A^t = S$. We have that

$$e_j = \sum_n C^e_{jn} D_n$$

and

$$f_k = \sum_m C^f_{km} D_m,$$

where e_j and f_k are the j-th 'edge' and k-th 'face' basis functions and D_n and D_m are members of the orthogonalised atomic orbital basis set. It follows that $S(e_j, f_k) = \sum_n C^e_{jn} \cdot C^f_{kn}$ where $S(e_j, f_k)$ is the overlap integral between e_j and f_k.

Now,

$$e_j = \sum_s c^e_{js} M^e_s$$

and

$$M^e_s = \sum_n c^e_{sn} D_n,$$

where M^e_s is a molecular orbital of symmetry species s, the coefficients c^e_{js} being symmetry determined.

If follows that,

$$C^e_{jn} = \sum_s \sum_n c^e_{js} \cdot c^e_{sn}$$

and, similarly,

$$C^f_{kn} = \sum_s \sum_n c^f_{ks} \cdot c^f_{sn}.$$

Hence,

$$S(e_j, f_k) = \sum_s \sum_n c^e_{js} \cdot c^e_{sn} \cdot c^f_{ks} \cdot c^f_{sn} = \sum_s \sum_n (c^e_{js} c^f_{ks}) \cdot (c^e_{sn} c^f_{sn}). \qquad (3)$$

Consider the second bracket in (3). If we arrange the symmetry adapted functions derived from 'edge' and 'face' bases so that there is an ordered $1:1$ mapping between them (putting all $c^f_{sn} = 0$ when a function in the edge basis does not have a counterpart in the face basis, and vice versa), then if both 'edge' and 'face' bases are to lead to identical eigenfunctions we require that $c^e_{sn} = c^f_{sn}$, provided that neither is zero. In the latter case the product $c^e_{sn} \cdot c^f_{sn}$ makes no contribution to the summation (3). It follows that

$$\sum_n c^e_{sn} c^f_{sn} = 1 \text{ for all symmetry species, } s, \text{ subtended by both bases (normalization)}$$

(3) becomes

$$S(e_j, f_k) = \sum_s c^e_{js} \cdot c^f_{ks}. \tag{4}$$

Eq. (4) shows that when edge and face bases lead to identical molecular eigen-functions the overlap between the two bases is independent both of the mixing coefficients in T and of the basis set A; it is an invariant of the system. This arises because, for example, if the mixing coefficients are $\cos\theta$ and $\sin\theta$, expression (4) leads to a summation in which θ appears as the factor $(\cos^2\theta + \sin^2\theta)$.

Because of Eq. (4) we shall only consider 'face' topological basis sets in the present communication.

We have used Eq. (1) to analyse the 'face' bases of the B_4 tetrahedron and B_6 octahedron. These species are the simplest polyhedra to which the theory may be applied and, although particular examples, provide an indication of the transferability of the topological coulomb and resonance integral parameters, α and β. It should be noted that for these two species the requirement that the members of each basis are as localised as possible leads to the complete localization of each member in a corresponding face.

We have chosen to work with Slater-type atomic orbitals since the consequent overlap integrals are very similar to those obtained for SCF functions. The boron-boron internuclear distance has been taken as constant at 1.70 Å.

Results

The expansion of a topological 'face' orbital in terms of its atomic orbital components is given in Table 1 for tetrahedral and octahedral cases. The calculation of these values is detailed in an Appendix. These expansions, together with the assumption of coulomb integrals $\alpha_{2s}(B) = -15.4, \alpha_{2p}(B) = -8.6, \alpha_{3d}(B) = -1.0$ eV [8] and resonance integrals given by $\beta_{ij} = KS_{ij}, K = -21$ eV leads to the para-meters values $\alpha_{oct} = -12.2$ eV, $\alpha_{tet} = -14.7$ eV, $\beta_{oct} = -2.6$ eV and $\beta_{tet} = -1.9$ eV. A comparison between the molecular orbital energy level sequences obtained using these values and those found by Lipscomb et al. [9] (using identical values for the atomic orbital coulomb and resonance integral parameters) is given in Table 2.

The overlap integral between members of the two basis sets was found to be 0.79, evaluated by transforming the tetrahedral basis set onto octahedral axes.

Discussion

It is probable that the difference between localised three-centre 'face' orbitals in the octahedron and tetrahedron will be greater than that for closely related molecules, such as those 'basket' boron hydrides which are icosahedral 'fragments'. For instance, a boron s-orbital participates in four 'face' orbitals in the octahedron but in only three in the tetrahedron. One consequence of this difference is the considerable d-orbital participation found for the octahedron. The difficulty in choice of coulomb, resonance and overlap integrals appropriate to d-orbital interactions is reflected in the α_{oct} and β_{oct} values. Even so, the data, coupled

Table 1. *The topological 'face' A orbitals in terms of atomic orbital components for the tetrahedron (atoms 2, 3 and 4) and octahedron (atoms 1, 2 and 3)*; $\sigma = \dfrac{1}{\sqrt{2}}(s + p_z)$

	Tetrahedron	Octahedron	
		0.3966	σ_1
σ_1	0	0.3966	σ_2
σ_2	0.3710	0.3966	σ_3
σ_3	0.3710	0	σ_4
σ_4	0.3710	0	σ_5
		0	σ_6
		-0.6520	π_{1x}
		0	π_{2x}
		-0.6520	π_{3x}
π_{1v}	0	0	π_{4x}
π_{2v}	-0.7341	0	π_{5x}
π_{3v}	-0.3671	0	π_{6x}
π_{4v}	-0.3671	-0.6520	π_{1y}
		-0.6520	π_{2y}
		0	π_{3y}
		0	π_{4y}
π_{1h}	0	0	π_{5y}
π_{2h}	0	0	π_{6y}
π_{3h}	0.6358	0	π_{1z}
π_{4h}	-0.6358	0.6520	π_{2z}
		0.6520	π_{3z}
		0	π_{4z}
		0	π_{5z}
		0	π_{6z}
		0.8166	δ_1
		0.8166	δ_2
		0.8166	δ_3
		0	δ_4
		0	δ_5
		0	δ_6

Table 2. *Face orbital energies (eV) for the B_6 octahedron and the B_4 tetrahedron*

	Ref. [9]	This work
Octahedron		
A_{2u}		-4.4
E_g	68.2	
T_{2u}	-2.6	
T_{2g}	-13.8	-9.6
T_{1u}	-15.7	-14.8
A_{1g}	-18.3	-20.0
Tetrahedron		
E	-10.6	
T_2	-14.7	-12.8
A_1	-17.5	-20.4

with the overlap integral of 0.79 between 'face' orbitals in the two bases, is good enough to make it clear that only a very crude transferability exists between the two systems. That is, there may be significant differences between the 'three-centred bonds' appropriate to different polyhedral systems. Granted that this is so, the question remains of whether topological bases provides a useful semi-quantitative picture of the bonding in the boron hydrides. Table 2 is of interest in this connection. In this table we compare the molecular orbital energy-level sequence found by Longuet-Higgins and Roberts and Hoffman and Lipscomb, who used an explicit AO basis, respectively, for an octahedron and tetrahedron of boron atoms. Our approach predicts a larger energy separation between the molecular orbital energies with agreement between the two methods on their relative order. In order to compare our results with theirs we have used $\alpha = -10.4\,\text{eV}$ and $K = -21\,\text{eV}$ in evaluating their orbital energies using $E = \dfrac{-\alpha - Kx}{1 + x}$. This value of α (assumed identical for s and p-functions) is the weighted mean of the values of α_{2s} and α_{2p} used in our own calculations. This procedure is in no way responsible for the large positive energy at which the explicit AO basis method places the lowest molecular orbital of E_g symmetry in the octahedron. This energy is the more disturbing in that Hoffman and Gouterman in their electron on a perturbed sphere model do not distinguish between the energy of this function and the T_{2g}, which is found to have an energy of $-13.8\,\text{eV}$. In that our MO energies are all negative (and one would expect this statement to be generally true) the three-centered bond approach seems to be preferable. Because of the small size of the basis set, some low lying virtual molecular orbitals are not generated by the method. This will undoubtedly be of importance in attempts to use the basis in an SCF treatment.

We conclude that the simple concept of localised three-centre bonding orbitals provides a useful description of the bonding in the polyhedral boranes and may, at some points, be better than a description using a larger atomic orbital basis set. For the next stage in the development, it would be particularly useful if a method can be found of evaluating electron repulsion integrals over topological basis sets without a formal transformation back to an atomic orbital basis. We are currently investigating this problem.

Appendix

a) Tetrahedral Basis

Representative boron group orbitals are detailed in Table 3, using the axes shown in Fig. 1. The explicit form of the overlap integrals included in Table 3 are given in Table 4, where it has been assumed that

$$\sigma_n = \frac{1}{\sqrt{2}}\left[s(n) + p_z(n)\right].$$

Table 3

$a_1(\sigma)$	$1/N_1(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
$t_2(\sigma)$	$1/N_2(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$
$t_2(\pi)$	$1/N_3(\pi_{1v} + \pi_{2v} + \pi_{3v} + \pi_{4v})$
$e(\pi)$	$1/N_4(\pi_{1v} + \pi_{2v} - \pi_{3v} - \pi_{4v})$

where:

$$N_1 = 2[1 + 3S_1]^{\frac{1}{2}} \qquad S_1 = \int \sigma_1 \sigma_2 \, d\tau$$
$$N_2 = 2[1 - S_1]^{\frac{1}{2}} \qquad S_2 = \int \pi_{1v} \cdot \pi_{2v} \cdot d\tau$$
$$N_3 = 2[1 + S_2 + 2S_3]^{\frac{1}{2}} \qquad S_3 = \int \pi_{1v} \cdot \pi_{3v} \, d\tau$$
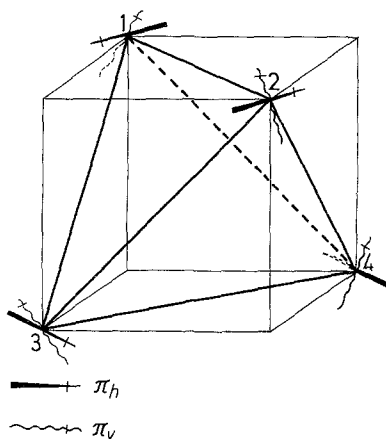$$N_4 = 2[1 + S_2 - 2S_3]^{\frac{1}{2}}$$

Fig. 1. Representative orbitals for the tetrahedron

Table 4

$$S_1 = \tfrac{1}{2}[S_\sigma(s,s) + 2\sqrt{\tfrac{2}{3}} \cdot S_\sigma(s,p) + \tfrac{1}{3}S_\pi(p,p) + \tfrac{2}{3}S_\sigma(p,p)]$$
$$S_2 = \tfrac{1}{3}[S_\sigma(p,p) + 2S_\pi(p,p)]$$
$$S_3 = \tfrac{1}{12}[7S_\pi(p,p) - S_\sigma(p,p)]$$

The required linear combination of the boron t_2 functions is of the form

$$\psi(t_2) = \frac{1}{(1 + \sin 2\theta \cdot S_4)^{\frac{1}{2}}} \left[\cos\theta \cdot \psi(T_2, \sigma) + \sin\theta \cdot \psi(T_2, \pi)\right]$$

where

$$S_4 = \frac{2S_5}{(1 - S_1)^{\frac{1}{2}}(1 + S_2 + 2S_3)^{\frac{1}{2}}}$$

and

$$S_5 = \frac{1}{\sqrt{6}} S_\sigma(s,p) + \frac{1}{3} S_\sigma(p,p) - \frac{1}{3} S_\pi(p,p).$$

The final expression relating the face bases $\{(A),(B),(C),(D)\}$, where (A) is the function corresponding to the face defined by the atoms 2, 3, and 4 is

$$
\begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} c & d & d & d & e & f & h & h & o & o & -g & g \\ d & d & d & c & f & e & h & h & o & o & g & -g \\ d & d & c & d & -h & -j & -e & -f & g & -g & o & o \\ d & c & d & d & -h & -h & -f & -e & -g & g & o & o \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \pi_{1v} \\ \pi_{2v} \\ \pi_{3v} \\ \pi_{4v} \\ \pi_{1h} \\ \pi_{2h} \\ \pi_{3h} \\ \pi_{4h} \end{pmatrix}
$$

where

$$
c = \left(\frac{1}{2N_1} + \frac{3a}{2N_2} \right), \quad e = \frac{b}{2} \left(\frac{1}{N_3} - \frac{2\sqrt{3}}{N_6} \right), \quad g = \frac{2\sqrt{3}b}{N_6}
$$

$$
d = \left(\frac{1}{2N_1} - \frac{a}{2N_2} \right), \quad f = \frac{b}{2} \left(\frac{1}{N_3} + \frac{2\sqrt{3}}{N_6} \right), \quad h = \frac{b}{N_3}
$$

$$
a = \frac{\cos\theta}{(1 + \sin 2\theta \cdot S_4)^{\frac{1}{2}}} \quad b = \frac{\sin\theta}{(1 + \sin 2\theta \cdot S_4)^{\frac{1}{2}}} ,
$$

$$
N_6 = [8 - 6S_6 - 2S_2]^{\frac{1}{2}}
$$

and

$$
S_6 = - S_\pi(p, p) .
$$

The condition of zero contribution of orbitals centered on atom 1 leads to the condition that

$$
\frac{1}{N_1} + \frac{3\cos\theta}{(1 + \sin 2\theta \cdot S_4)^{\frac{1}{2}} \cdot N_2} = 0
$$

whence

$$
\theta = 84°20'
$$

and

$$
\begin{array}{ll} c = 0 & f = -0.7341 \\ d = 0.3710 & g = -0.6358 \\ e = 0 & h = -0.3671 . \end{array}
$$

b) Octahedral Basis

Representative functions of the boron group orbitals are detailed in Table 5, and the explicit form of the overlap integrals are given in Table 6. Fig. 2 denotes the axes used. Again it has been assumed that

$$
\sigma_n = \frac{1}{\sqrt{2}} (s(n) + p_z(n)) .
$$

Table 5

$$a_{1g}(\sigma) = 1/N_1 \ (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$
$$e_g(\sigma) = 1/N_2 \ (\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5)$$
$$t_{1u}(\sigma) = 1/N_3 \ (\sigma_1 - \sigma_6)$$
$$t_{1u}(\pi) = 1/N_4 \ (\pi_{22} + \pi_{32} + \pi_{42} + \pi_{52})$$
$$t_{2g}(\pi) = 1/N_5 \ (\pi_{5x} + \pi_{4y} - \pi_{3x} - \pi_{2y})$$
$$t_{2g}(\delta) = 1/N_6 \ (\delta_1 + \delta_6)$$
$$t_{1g}(\pi) = 1/N_7 \ (\pi_{2y} + \pi_{5x} - \pi_{4y} - \pi_{3x})$$
$$t_{2u}(\pi) = 1/N_8 \ (\pi_{22} - \pi_{32} + \pi_{42} - \pi_{52})$$
$$a_{2u}(\delta) = 1/N_9 \ (\delta_1 - \delta_2 - \delta_3 + \delta_4 + \delta_5 - \delta_6)$$
$$e_u(\delta) = 1/N_{10}(\delta_2 - \delta_3 - \delta_4 + \delta_5) .$$

where
$$N_1 = \sqrt{6}\,(1 + 4S_1 + S_2)^{\frac{1}{2}} \qquad S_1 = \int \sigma_1 \cdot \sigma_2 d\tau$$
$$N_2 = 2\,(1 - 2S_1 + S_2)^{\frac{1}{2}} \qquad S_2 = \int \sigma_1 \sigma_6 d\tau$$
$$N_3 = \sqrt{2}\,(1 - S_2)^{\frac{1}{2}} \qquad S_3 = \int \pi_{1x} \cdot \pi_{3x} d\tau$$
$$N_4 = 2\,(1 + 2S_3 + S_4)^{\frac{1}{2}} \qquad S_4 = \int \pi_{1x} \cdot \pi_{6x} d\tau$$
$$N_5 = 2\,(1 + 2S_6 - S_4)^{\frac{1}{2}} \qquad S_5 = \int \sigma_1 \cdot \pi_{22} d\tau$$
$$N_6 = \sqrt{2}\,(1 + S_8)^{\frac{1}{2}} \qquad S_6 = \int \pi_{5x} \cdot \pi_{4y} \cdot d\tau$$
$$N_7 = 2\,(1 - 2S_6 - S_4)^{\frac{1}{2}} \qquad S_7 = \int \delta_1 \delta_4 d\tau$$
$$N_8 = 1\,(1 - 2S_3 + S_4)^{\frac{1}{2}} \qquad S_8 = \int \delta_1 \delta_6 d\tau$$
$$N_9 = \sqrt{6}\,(1 + 4S_7 - S_8)^{\frac{1}{2}} \qquad S_9 = \int \delta_1 \cdot \pi_{5x} d\tau$$
$$N_{10} = 2\,(1 - 2S_7 - S_8)^{\frac{1}{2}}$$

Table 6 [a]

$$S_1 = \tfrac{1}{2}[S_\sigma(s, s) + \sqrt{2}\,S_\sigma(s, p) + \tfrac{1}{2}[S_\sigma(p, p) + S_\pi(p, p)]]$$
$$S_2 = \tfrac{1}{2}[S'_\sigma(s, s) + 2S'_\sigma(s, p) + S'_\sigma(p, p)]$$
$$S_3 = S_\pi(p, p)$$
$$S_4 = S'_\pi(p, p)$$
$$S_5 = 2\,\frac{1}{\sqrt{2}}\,[\sqrt{2}\,S_\sigma(s, p) + S_\sigma(p, p) + S_\pi(p, p)]$$
$$S_6 = \tfrac{1}{2}[S_\sigma(p, p) + S_\pi(p, p)]$$
$$S_7 = \tfrac{1}{2}[S_\pi(d, d) + S_\delta(d, d)]$$
$$S_8 = S'_\delta(d, d)$$
$$S_9 = \frac{1}{\sqrt{2}}\,S_\pi(p, d)$$

[a] $S_\sigma, S_\pi, S_\delta$ overlaps refer to a boron-boron internuclear distance of 1.7 Å. $S'_\sigma, S'_\pi, S'_\delta$ refer to those of $\sqrt{2} \times 1.7$ Å.
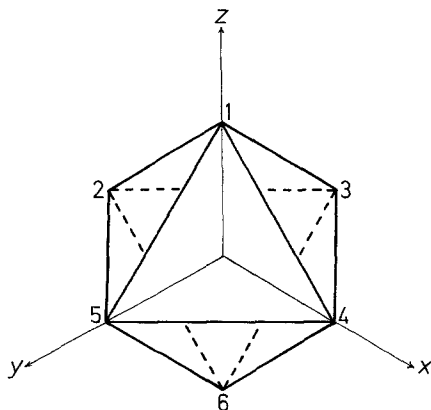

Fig. 2. Representative axes for octahedron

The required linear combination of the boron t_{1u} functions is of the form

$$\psi(t_{1u}) = \frac{1}{(1 + \sin 2\theta \cdot S_{10})^{\frac{1}{2}}} \left[\cos \theta \cdot \psi(T_{1u}, \sigma) + \sin \theta \cdot \psi(T_{1u}, \pi) \right]$$

where

$$S_{10} = \frac{4 S_5}{\sqrt{2} \, (1 - S_2)^{\frac{1}{2}} \cdot (1 + 2 S_3 + S_4)^{\frac{1}{2}}}$$

and those for the t_{2g} functions

$$(t_{2g}) = \left[\cos \phi \cdot \psi(T_{2g}, \pi) + \sin \phi \cdot \psi(T_{2g}, \delta) \right]$$

where we have assumed that $\int (T_{2g}, \pi)(T_{2g}, \delta) d\tau = 0$.

The final expression relating the face basis $\{(A), (B), (C), (D), (E), (F)\}$, where (A) is the function corresponding to the face defined by the atoms $1, 2,$ and 3, is

$$
\begin{pmatrix} A \\ B \\ C \\ D \\ E \\ F \end{pmatrix} =
\begin{pmatrix}
eeefff & -ho-hogg & -h-hogog & ohh-g-go & kkklll \\
efeeff & hoh-o-g-g & -h-go-hog & o-gh-h-go & klkkll \\
effeef & ho-goh-g & h-goho-g & o-g-ghho & kllkkl \\
eeffef & -hogo-hg & hho-go-g & oh-g-gho & kkllkl \\
feeffe & go-hog-h & g-hogo-h & o-h-hggo & lkkllk \\
ffeefe & -goho-gh & ggo-ho-h & og-h-hgo & llkklk \\
fffeee & -go-gohh & -g-gohoh & ogg-h-ho & lllkkk \\
feffee & gogo-h-h & -gho-goh & o-hgg-ho & lkllkk
\end{pmatrix}
\begin{pmatrix} \sigma_1 \\ \vdots \\ \sigma_6 \\ \pi_{1x} \\ \vdots \\ \pi_{6x} \\ \pi_{1y} \\ \vdots \\ \pi_{6y} \\ \pi_{1z} \\ \vdots \\ \pi_{6z} \\ \delta_1 \\ \vdots \\ \delta_6 \end{pmatrix}
$$

where

$$e = \frac{1}{N_1} + \frac{a}{N_4}$$

$$f = \frac{1}{N_1} - \frac{a}{N_4}$$

$$g = \frac{-b}{N_5} + \frac{c}{N_6}$$

$$h = \frac{b}{N_5} + \frac{c}{N_6}$$

$$k = \frac{d}{N_{10}} + \frac{1}{N_9}$$

$$l = \frac{d}{N_{10}} - \frac{1}{N_9}.$$

$$a = \frac{\cos \theta}{(1 + \sin 2\theta \cdot S_{10})^{\frac{1}{2}}}$$

$$b = \frac{\sin \theta}{(1 + \sin 2\theta \cdot S_{10})^{\frac{1}{2}}}$$

$$c = \cos \phi$$

$$d = \sin \phi$$

The condition of zero contribution of orbitals centred on atom 4, 5, and 6 to (A) leads to values of θ and ϕ of

$$\theta = 76°44' \text{ and } \phi = 36°0'$$

whence $\quad e = 0.3966$

$$f = 0$$

$$g = 0$$

$$h = 0.6520$$

$$k = 0.8166$$

$$l = 0 \, .$$

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Prof. S. F. A. Kettle
School of Chemical Sciences
University of East Anglia
University Plain
Norwich NOR 88 C, England