

THREE-DIMENSIONAL AROMATICITY: A TOPOLOGICAL ANALYSIS OF COMPUTATIONAL METHODS

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Abstract

The deltahedral boranes $B_n H_n^{2-}$ ($6 \leq n \leq 12$) may be regarded as three-dimensional delocalized aromatic systems in which surface bonding and core bonding correspond to σ -bonding and π -bonding, respectively, in planar polygonal two-dimensional hydrocarbons $C_n H_n^{(n-6)+}$ ($n = 5, 6, 7$). The two extreme types of topologies which may be used to model core bonding in deltahedral boranes are the deltahedral (D_n) topology based on the 1-skeleton of the underlying deltahedron and the complete (K_n) topology based on the corresponding complete graph. Symmetry factoring of generalized graphs representing the core-bonding interactions in the highly symmetrical octahedral borane $B_6 H_6^{2-}$ and icosahedral borane $B_{12} H_{12}^{2-}$ leads to methods for separating the effects of core and surface bonding in molecular orbital energy parameters. Such analyses of the Hoffmann–Perkins–Stewart self-consistent molecular orbital computations, the Armstrong–Perkins–Stewart self-consistent molecular orbital computations, and SCF MO ab initio Gaussian 82 computations on $B_6 H_6^{2-}$ and $B_{12} H_{12}^{2-}$ indicate that the approximation of atomic orbitals by a sum of Gaussians, as is typical in modern ab initio computations, leads to significantly weaker apparent core bonding approximated more closely by deltahedral (D_n) rather than complete (K_n) topology. Furthermore, the T_{1u} core orbitals which, if pure, would be non-bonding in octahedral (D_6) core topology for $B_6 H_6^{2-}$ and bonding in icosahedral (D_{12}) core topology for $B_{12} H_{12}^{2-}$, become antibonding through strong core–surface mixing. Because of this, the simpler graph-theory derived model for deltahedral boranes using complete (K_n) core bonding topology gives the correct numbers of bonding orbitals even in cases where the complete graph K_n is a poor approximation for the actual core bonding topology.

1. Introduction

The concepts of resonance energy and aromaticity as originally arising from molecular orbital theory [1–3] and subsequently refined through graph-theoretical methods [4–6] are central to the chemical bonding theory of two-dimensional planar hydrocarbons and heterocycles. More recently, similar ideas have been shown to be applicable to the chemical bonding of the three-dimensional polyhedral boranes $B_n H_n^{2-}$ ($6 \leq n \leq 12$) [7], in which the boron atoms form the deltahedra with no degree 3 vertices depicted in fig. 1. In 1977, we first used qualitative graph-theoretical methods to demonstrate the analogy between the chemical bonding topology in two-dimensional planar aromatic hydrocarbons and that in three-dimensional deltahedral boranes [8]. A similar approach was also shown to provide useful information on the structure and bonding of diverse transition metal [9–11] and post-transition metal [12, 13] clusters with minimal

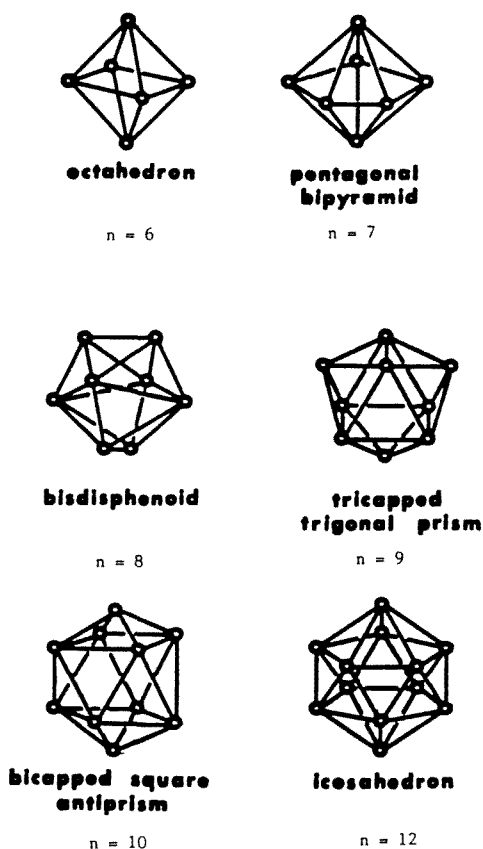


Fig. 1. Deltahedra without degree 3 vertices found in the borane anions $B_n H_n^{2-}$ ($n = 6, 7, 8, 9, 10, \text{ and } 12$).

need for computation. More recently, related ideas have been applied to various superconductors [14,15], including the high T_c copper oxides [15,16].

The virtual absence of computation required for implementation of our graph-theory derived method for the treatment of the chemical bonding topology in polyhedral boranes and metal clusters has facilitated its application to an extensive variety of diverse systems. The wide applicability of the graph-theory derived method makes of interest its comparison with various other approaches requiring substantial amounts of computation for the treatment of the same systems. The energy parameters of the molecular orbitals, both bonding and antibonding, provide a basis for making such comparisons, subject to the following limitations:

- (1) Energy parameters of *all* molecular orbitals, both bonding and antibonding, are required for meaningful comparisons to be made, thereby precluding the use of essentially all computations published before 1975, which do not provide the necessary energy parameters for the unfilled antibonding (virtual) molecular orbitals.

- (2) Such comparisons have been limited to the polyhedral boranes, since the presence of d orbitals in transition metal valence shells has prevented effective comparisons for transition metal clusters.
- (3) More detailed and reliable comparisons can be made on systems of high symmetry with fewer distinct molecular orbital energy parameters, i.e. higher average molecular orbital degeneracies.

Our initial work [17] used the 1962 LCAO-MO extended Hückel computations by Hoffmann and Lipscomb [18] on $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$. Subsequent work [19] has extended this comparison to some less symmetrical deltahedral boranes, as well as to self-consistent but still semiempirical molecular orbital computations by Armstrong, Perkins, and Stewart [20]. More recently, in collaboration with Dai and Gimarc [21], we have applied this approach to ab initio SCF MO Gaussian 82 computations with an STO-3G basis set in order to provide some insight into the effect on the apparent chemical bonding topology in deltahedral boranes when atomic orbitals are approximated by Gaussians. This paper describes our method for the topological analysis of the results from such computations on deltahedral boranes. In this paper, the analysis is limited to the regular polyhedral anions $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, where favorable symmetry allows maximum information to be obtained, as noted above.

2. Topological background

Topological ideas can be used to describe the Hückel theory as it has been traditionally applied to conventional two-dimensional aromatic systems [22–25], of which benzene is generally regarded as the prototype. The overlap of the atomic orbitals involved in the delocalized bonding in aromatic systems can be represented by a graph in which the vertices correspond to the orbitals and the edges correspond to orbital overlaps. The adjacency matrix [26] of such a graph can be defined as follows:

$$A_{ij} = 0, \quad \text{if } i = j; \tag{1a}$$

$$A_{ij} = 1, \quad \text{if } i \text{ and } j \text{ are connected by an edge}; \tag{1b}$$

$$A_{ij} = 0, \quad \text{if } i \text{ and } j \text{ are not connected by an edge}. \tag{1c}$$

The eigenvalues of the adjacency matrix are obtained from the following determinantal equation:

$$|A - xI| = 0, \tag{2}$$

where I is the unit matrix ($I_{ii} = 1$ and $I_{ij} = 0$ for $i \neq j$). These topologically derived eigenvalues are closely related to the energy levels as determined by the Hückel theory [22–25], which uses the secular equation

$$|H - ES| = 0. \quad (3)$$

In eq. (3), the energy matrix H and the overlap matrix S can be resolved into the unit matrix I and the adjacency matrix A as follows:

$$H = \alpha I + \beta A, \quad (4a)$$

$$S = I + SA. \quad (4b)$$

The energy levels of the Hückel molecular orbitals (eq. (3)) are thus related to the eigenvalues x_k of the adjacency matrix A (eq. (2)) by the following equation:

$$E_k = \frac{\alpha + x_k \beta}{1 + x_k S}, \quad (5)$$

where α is the standard Coulomb integral, assumed to be the same for all atoms, β is the resonance integral, taken to be the same for all bonds, and S is the overlap integral between atomic orbitals on neighboring atoms.

A difficulty in applying eq. (5) is the need to determine the three parameters α , β , and S to relate the eigenvalues x_k determined from pure topological considerations to the corresponding Hückel molecular orbital energies E_k . Our qualitative graph-theory derived approach considers only the topological contribution to the molecular orbital energies, i.e.

$$E_k \approx x_k \beta, \quad (6)$$

so that E_k is measured relative to the center point α , S is taken to be zero, and β is an energy unit derivable from experimental data or, in the case of this work, from molecular orbital energies computed by some other method. Reduction of eq. (5) to eq. (6) by setting S to zero implies that the energies E_k are directly proportional to the eigenvalues x_k of the adjacency matrix. As long as S is zero or positive, positive values of x_k correspond to bonding orbitals and negative values of x_k correspond to antibonding orbitals. In addition, the center point α corresponding to a given computation can be calculated from the midpoint of *all* of the molecular orbital energy parameters (bonding, nonbonding, and antibonding) by taking a degeneracy weighted average, i.e.

$$\alpha = \frac{\sum_k g_k E_k}{\sum_k g_k}, \quad (7)$$

where g_k is the degeneracy of energy level E_k and the summation is over *all* orbitals k .

The two extreme types of skeletal chemical bonding in molecules formed by polygonal or polyhedral clusters of atoms including planar aromatic hydrocarbons and

polyhedral boranes, as well as metal clusters, may be called *edge-localized* and *globally delocalized* [8–11]. An edge-localized polygon or polyhedron has two-electron two-center bonds along each edge, and is favored when the number of internal orbitals from each vertex atom matches the degree of the corresponding vertex. A globally delocalized polygon or polyhedron has a multicenter bond involving all of the vertex atoms; such global delocalization is a feature of fully aromatic systems, whether two-dimensional such as benzene or three-dimensional such as the deltahedral borane anions $B_n H_n^{2-}$ ($6 \leq n \leq 12$). Such delocalization is favored when the numbers of internal orbitals do *not* match the vertex degrees. Fully globally delocalized polyhedra are *deltahedra*, namely, polyhedra in which all faces are triangles. A distinctive feature of such deltahedra with n vertices is an n -center core bond in the center of the deltahedron. The four valence orbitals of vertex boron atoms in the $B_n H_n^{2-}$ deltahedral borane anions, as well as those of the vertex carbon atoms in the planar polygonal hydrocarbons $C_n H_n^{(n-6)+}$ ($n = 5, 6, 7$) and the polyhedranes $C_{2n} H_{2n}$, are partitioned into one external orbital for bonding to hydrogen or another external group and three internal orbitals for the skeletal bonding. For the planar polygons $C_n H_n^{(n-6)+}$ ($n = 5, 6, 7$), the vertex degrees are all two and thus do not match the available three internal orbitals thereby leading to globally delocalized two-dimensional aromatic systems. For the polyhedranes $C_{2n} H_{2n}$ such as tetrahedrane ($n = 2$), cubane ($n = 4$), and dodecahedrane ($n = 10$), the vertex degrees are all three which match the three available internal orbitals leading to edge-localized bonding. For the deltahedral borane anions $B_n H_n^{2-}$ ($6 \leq n \leq 12$), the vertex degrees are all four or larger and thus do not match the available three internal orbitals thereby leading to globally delocalized three-dimensional aromatic systems.

A major achievement of the graph-theory derived approach to the chemical bonding topology of globally delocalized systems is the demonstration of the close analogy between the bonding in two-dimensional planar aromatic systems such as benzene and that in three-dimensional deltahedral boranes and carboranes [8–11]. In such a system with n vertices, the three internal orbitals on each vertex atom are partitioned into two twin internal orbitals (called *tangential* in some other methods [27]) and a unique internal orbital (called *radial* in some other methods [27]). Pairwise overlap between the $2n$ twin internal orbitals is responsible for the formation of the polygonal or deltahedral framework and leads to the splitting of these $2n$ orbitals into n bonding and n antibonding orbitals. The magnitude of this splitting is designated as $2\beta_s$, where β_s relates to the parameter β in eqs. (4a), (5), and (6). This portion of the chemical bonding topology can be described by a disconnected graph G_s having $2n$ vertices corresponding to the $2n$ twin internal orbitals and n isolated K_2 components; a K_2 component has only two vertices joined by a single edge. The dimensionality of this bonding of the twin internal orbitals is one less than the dimensionality of the globally delocalized system [11]. Thus, in the case of the two-dimensional planar polygonal systems, the pairwise overlap of the $2n$ twin internal orbitals leads to the σ -bonding network, which may be regarded as a collection of n one-dimensional bonds along the perimeter of the polygon involving adjacent pairs of polygonal vertices. The n bonding and n antibonding orbitals correspond to the σ -bonding and σ^* -antibonding orbitals,

respectively. In the case of the three-dimensional deltahedral systems, the pairwise overlap of the $2n$ twin internal orbitals results in bonding over the two-dimensional surface of the deltahedron, which may be regarded as topologically homeomorphic [28] to the sphere.

The equal numbers of bonding and antibonding orbitals formed by pairwise overlap of the twin internal orbitals are supplemented by additional bonding and antibonding orbitals formed by global mutual overlap of the n unique internal orbitals. This bonding topology can be represented by a graph G_c in which the vertices correspond to the vertex atoms of the polygon or deltahedron, or equivalently their unique internal orbitals, and the edges represent pairs of overlapping unique internal orbitals. The relative energies of the additional molecular orbitals arising from such overlap of the unique internal orbitals are determined from the eigenvalues of the adjacency matrix A_c of the graph G_c using β or, more specifically, β_c , as the energy unit (eqs. (4a), (5), and (6)). In the case of the two-dimensional aromatic system benzene, the graph G_c is the C_6 cyclic graph (the 1-skeleton [29] of the hexagon) which has three positive and three negative eigenvalues corresponding to the three π -bonding and three π^* -antibonding orbitals, respectively. The spectra of the cyclic graphs C_n all have odd numbers of positive eigenvalues [30], leading to the familiar $4k + 2$ ($k = \text{integer}$) π -electrons [31] for planar aromatic hydrocarbons.

A critical question is the nature of the core bonding graph G_c for the deltahedral boranes $B_nH_n^{2-}$. The two limiting possibilities for G_c are the complete graph K_n and the deltahedral graph D_n , and the corresponding core bonding topologies can be called the *complete* and *deltahedral* topologies, respectively. In the complete graph K_n , each vertex has an edge going to every other vertex, leading to a total of $n(n-1)/2$ edges [32]. For any value of n , the complete graph K_n has only one positive eigenvalue, namely, $n-1$, and $n-1$ negative eigenvalues, namely, -1 each. The deltahedral graph D_n is identical to the 1-skeleton [29] of the deltahedron. Thus, two vertices of D_n are connected by an edge if, and only if, the corresponding vertices of the deltahedron are connected by an edge. The graph D_n for the deltahedra of interest with seven or more vertices all have at least three positive eigenvalues. However, in all cases there is a unique positive eigenvalue which is much more positive than any other of the positive eigenvalues. This unique positive eigenvalue, conveniently called the *principal eigenvalue*, arises from the fully symmetric pathway of the symmetry factoring scheme [33] used to determine the eigenvalues of D_n , namely, the pathway using G_g components at branches from twofold symmetry operations and G_a components at branches from threefold symmetry operations. The molecular orbital corresponding to the principal eigenvalue of G_c may be called the *principal core orbital*. Since deltahedral boranes of the stoichiometry $B_nH_n^{2-}$ have $2n + 2$ skeletal electrons, of which $2n$ are used for the surface bonding, there are only two skeletal electrons available for core bonding, corresponding to a single core bonding molecular orbital and a single positive eigenvalue for G_c . Thus, deltahedral boranes are three-dimensional aromatic systems with $4k + 2 = 2$ core bonding electrons where $k = 0$, analogous to the $4k + 2$ π -electrons where $k = 0$ ($C_3H_3^+$), 1 ($C_5H_5^-$, C_6H_6 , $C_7H_7^+$) or 2 ($C_8H_8^{2-}$) for planar two-dimensional

aromatic systems. Furthermore, only if G_c is taken to be the corresponding complete graph K_n will the simple model given above for globally delocalized deltahedra give the correct number of skeletal electrons in all cases, namely, $2n + 2$ skeletal electrons for $6 \leq n \leq 12$. Such a model with complete core bonding topology is the basis for the graph-theory derived model for the chemical bonding topology of deltahedral boranes and metal clusters discussed in previous papers [8–11]. However, deltahedral core bonding topology can also account for the observed $2n + 2$ skeletal electrons in the $B_n H_n^{2-}$ deltahedral boranes if there is a mechanism for raising the energies of all the core molecular orbitals other than the principal core orbital to antibonding energy levels. This possibility was already indicated in the original graph-theoretical analysis [17] of the $3n$ Hoffmann–Lipscomb LCAO-MO extended Hückel computations [18] on icosahedral $B_{12} H_{12}^{2-}$, which showed that four core orbitals would be bonding orbitals except for core–surface orbital mixing which raises the energies of three of these four core orbitals to antibonding levels, leaving only the principal core orbital as a bonding core orbital.

The distinction between complete (K_n) and deltahedral (D_n) core bonding topology is most clearly explained for octahedral $B_6 H_6^{2-}$. Among the fifteen pairs of six vertices in an octahedron (D_6 graph), twelve pairs correspond to edges of the octahedron (*cis* interactions), and the remaining three pairs correspond to antipodal vertices related by the inversion center and *not* connected by an edge (*trans* interactions). However, all of the fifteen pairs of six vertices in a complete K_6 graph correspond to edges of equal weight. In an octahedral array of six points, a parameter t can be defined as the ratio of the *trans* interactions to the *cis* interactions. This parameter t is 0 for the pure octahedral topology (D_6) and 1 for pure complete topology (K_6). Values of t between 0 and 1 can be used to measure gradations of topologies between D_6 and K_6 , corresponding to the weighting of edges representing *trans* interactions relative to those representing *cis* interactions in the underlying graph. In group-theoretical terms, pure complete core bonding topology (i.e. $t = 1$) uses the symmetric group [34] S_6 with 720 operations (i.e. the automorphism group of the complete graph K_6) rather than its subgroup O_h with 48 operations (i.e. the point group of the octahedron) to represent the symmetry of the core bonding manifold in $B_6 H_6^{2-}$. The actual O_h rather than S_6 symmetry of these systems will result in partial removal of the fivefold degeneracy of the core antibonding orbitals implied by the complete core bonding topology. The value of the parameter t corresponding to a given computation on octahedral $B_6 H_6^{2-}$ can be estimated from the energy parameters computed for the A_{1g} and E_g core molecular orbitals [17, 19]. The core bonding topology corresponding to a given computation on $B_6 H_6^{2-}$ can thus be determined.

These ideas concerning the skeletal bonding in deltahedral borane anions can be related to tensor surface harmonic theory as developed by Stone [35] and elaborated by Mingos and Johnston [36]. The n core orbitals may be described by the scalar spherical harmonics, which for deltahedra having n vertices correspond successively to the single S^σ , the three P^σ , the five D^σ , the seven F^σ orbitals, etc., of increasing energy and nodality. The surface orbitals may be described by the vector spherical harmonics,

which for deltahedra having n vertices correspond successively to three P^π , five D^π , seven F^π bonding/antibonding orbital pairs, etc., of increasing energy and nodality. This relates to the following aspects of the graph-theory derived model for the skeletal bonding in deltahedral boranes:

- (1) The principal core orbital corresponds to the S_s^σ orbital in tensor surface harmonic theory. Since there are no S_p^π or \bar{S}_p^π surface orbitals, the principal core orbital (S_s^σ) cannot mix with any of the surface orbitals, in accord with ideas discussed above. Thus, the principal core orbital cannot be made antibonding through core-surface mixing.
- (2) The three core orbitals of lowest energy other than the principal core orbital (S_s^σ) correspond to P_s^σ orbitals in tensor surface harmonic theory. These orbitals correspond to the three most positive eigenvalues other than the principal eigenvalue of the corresponding deltahedra. The P_s^σ core orbitals mix with the P_p^π surface orbitals so that the P_s^σ core orbitals become antibonding with corresponding lowering of the energies of the P_p^π surface orbitals below the energies of the other surface bonding orbitals. Thus, in computations of molecular orbital energies of the $B_n H_n^{2-}$ deltahedral borane anions, the lowest lying molecular orbital is the principal core orbital (S_s^σ) and the next lowest lying orbitals correspond to the three P^π surface orbitals, which will be degenerate in the case of octahedral $B_6 H_6^{2-}$ and icosahedral $B_{12} H_{12}^{2-}$ but not in the case of the less symmetrical deltahedra.

In order to relate a given computation on a deltahedral borane to topological models for its chemical bonding, all of its molecular orbital energy parameters are required, including those for the unfilled antibonding (virtual) orbitals, thereby precluding such an analysis for many of the published computations [37–41]. From such information, the first step is to calculate α , the energy "zero point" of eqs. (4a) and (5). The value of α corresponding to a given complete set of molecular orbital energy parameters is best determined by taking the degeneracy weighted average of the energy parameters for *all* of the molecular orbitals, as indicated in eq. (7). Next, the surface energy unit β_s can be estimated as the degeneracy weighted average distance of the pure surface orbitals from the energy zero point α . At this stage, sampling error is unavoidably introduced since the energy parameters of only the *pure* surface orbitals can be included in this average. The other surface orbitals must be excluded from this average since their energy parameters are distorted by substantial mixing with the core and external orbitals belonging to the same irreducible representations. The sign of the resulting β_s is the same as the sign of the bonding pure surface orbitals.

Further analysis of the computed molecular orbital energy parameters either requires some special symmetry such as that found in octahedral $B_6 H_6^{2-}$ or icosahedral $B_{12} H_{12}^{2-}$, or some further assumptions concerning the chemical bonding topology for the less symmetrical deltahedra. Only the former situation is discussed in this paper. In the cases of the systems with special symmetry, the core energy units β_c and the nonadjacent

atom unique internal orbital interactions (i.e. t in $B_6H_6^{2-}$ and m in $B_{12}H_{12}^{2-}$) can be estimated from the energy parameters of the principal core orbital and the other core orbital not mixing with surface orbitals. This method is subject to possible errors arising from core–external orbital interactions. However, a comparison of the Hoffmann–Lipscomb "3n", "4n", and "5n" computations [18] suggests that these core–external interactions are not large enough to cause serious errors.

3. Methods

Consider an octahedrally weighted K_6 complete graph having 12 edges of unit weight corresponding to the octahedron edges (*cis* interactions) and the remaining 3 edges of weight t corresponding to the three octahedron antipodal vertex pairs. The spectrum of this graph can be determined by symmetry factoring [33] using a threefold axis (fig. 2). The symmetric branch (A in fig. 2) gives the eigenvalue $4 + t$ corresponding to the A_{1g} principal core molecular orbital, as well as one of the $-t$ eigenvalues of

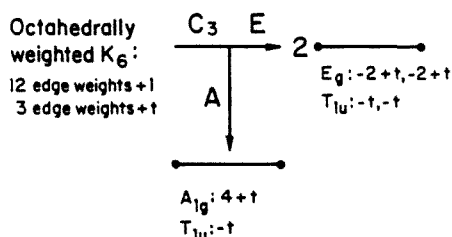


Fig. 2. Symmetry factoring scheme for an octahedrally weighted K_6 graph using a threefold axis (C_3) leading to A and E branches [33].

the triply degenerate T_{1u} core molecular orbital. The doubly degenerate E branch (fig. 2) gives the other two $-t$ eigenvalues of the triply degenerate T_{1u} core molecular orbital, as well as the two $-2 + t$ eigenvalues of the doubly degenerate E_g core molecular orbital. Note that any positive value of t (up to $+2$) is sufficient to lead to only one positive eigenvalue, namely the $4 + t$ eigenvalue of the A_{1g} orbital, and five negative eigenvalues, namely the $-t$ eigenvalues of the triply degenerate T_{1u} orbitals and the $-2 + t$ eigenvalues of the doubly degenerate E_g orbital. This indicates that any positive *trans* interaction in an octahedron gives the same distribution of bonding and antibonding orbitals, namely 1 and 5, respectively, as an unweighted (i.e. $t = 1$) K_6 graph. Thus, for octahedral boranes the numbers of bonding and antibonding orbitals are insensitive to the value taken for t . Note also that setting $t = 0$ leads to the spectrum of the octahedron $(+4, 0, 0, 0, -2, -2)$ which is the D_6 graph, whereas setting $t = 1$ leads to the spectrum of the K_6 complete graph $(+5, -1, -1, -1, -1, -1)$.

This symmetry factoring procedure indicates that in the absence of core–surface and core–external orbital mixing, the energy parameters of the octahedral core orbitals in $B_6H_6^{2-}$ relative to α are determined by the equations

$$E(A_{1g})_c = (4 + t)\beta_c, \quad (8a)$$

$$E(T_{1u})_c = -t\beta_c, \quad (8b)$$

$$E(E_g)_c = (-2 + t)\beta_c, \quad (8c)$$

where β_c is the core energy unit and t is the ratio of *trans* to *cis* interactions. The core octahedral orbitals not subject to core-surface mixing are the A_{1g} principal core orbital and the doubly degenerate E_g antibonding core orbitals. Furthermore, a comparison of the molecular orbital energy parameters from the $3n$, $4n$, and $5n$ computations on $B_6H_6^{2-}$ by Hoffmann and Lipscomb [18] suggests that core-external orbital mixing, unlike core-surface orbital mixing, is relatively minor in this system. Substitution of the energy parameters of the A_{1g} core orbital, readily recognized as by far the most strongly bonding molecular orbital, and an antibonding E_g orbital into eqs. (8a) and (8c), respectively, leads to two equations which can be solved for the two unknowns t and β_c . In cases where the two sets of antibonding E_g orbitals differ significantly in energy, only one of the two possible choices, namely the less antibonding E_g orbital, was found to give a physically reasonable positive value of t between 0 and 1. The E_g orbital giving such a positive value of t was therefore chosen to be the core orbital, leaving the more strongly antibonding E_g orbital to be an antibonding external orbital. The values of t and β_c so obtained by solving eqs. (8a) and (8c) can be substituted into eq. (8b) to give a hypothetical value for $E(T_{1u})_c$ in the absence of core-surface mixing. Comparison of this value with the computed value for the T_{1u} core orbital gives a parameter $\Delta E(T_{1u})$, which can be taken to measure the extent of core-surface mixing.

Related methods can be used to compare the computed octahedral surface orbital energy parameters with those arising from the graph-theory derived method. In this case, the ideal surface orbital energy parameters for the octahedron based on S_6 symmetry are determined by the equations

$$E(T_{2g}) = E(T_{1u})_s = \beta_s, \quad (9a)$$

$$E(T_{2u}) = E(T_{1g}) = -\beta_s, \quad (9b)$$

where β_s is the surface energy unit. Reduction of the effective symmetry from the S_6 automorphism group of the K_6 graph to the actual O_h point group of a regular octahedron will make $E(T_{2u})$ no longer equal to $E(T_{1g})$ and $E(T_{2g})$ no longer equal to $E(T_{1u})_s$. On the basis of eqs. (9a) and (9b), the following appropriately weighted mean of the energy parameters of the *pure* surface orbitals T_{2g} , T_{2u} , and T_{1g} can be used to determine β_s :

$$\beta_s = 1/2[-1/2(E(T_{2u}) + E(T_{1g})) + E(T_{2g})]. \quad (10)$$

The energy parameter $E(T_{1u})_s$ is not included in this mean because of the uncertainty in the core-surface mixing parameter $\Delta E(T_{1u})$, obtained as outlined above, which must be subtracted from the value of $E(T_{1u})_s$ obtained from the actual computation.

A similar approach can be used for the treatment of icosahedral boranes. Thus, consider an icosahedrally weighted K_{12} complete graph having 30 edges of unit weight corresponding to the icosahedron edges, 30 edges of weight m corresponding to the *meta* interaction of nonadjacent, nonantipodal vertex pairs, and 6 edges of weight p corresponding to the *para* interaction of the 6 icosahedron antipodal pairs. The spectrum of this graph can be determined by symmetry factoring [33] using first a threefold axis and then a twofold axis (fig. 3). The fully symmetric branch (AG) gives the eigenvalue

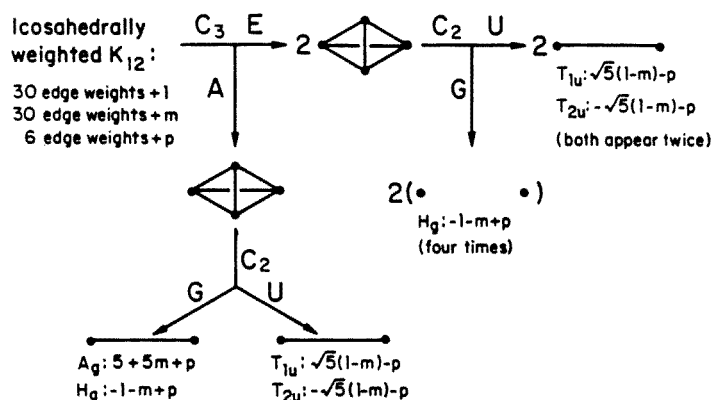


Fig. 3. Symmetry factoring scheme for an icosahedrally weighted K_{12} graph using first a threefold axis (C_3) leading to A and E branches, followed by a twofold axis (C_2) leading to G and U branches [33].

$5 + 5m + p$ corresponding to the A_g principal core molecular orbital, as well as one of the $-1 - m + p$ eigenvalues of the H_g quintuply degenerate core molecular orbitals. The remaining four $-1 - m + p$ eigenvalues of the quintuply degenerate H_g core molecular orbitals arise from the two isolated vertices of the doubly degenerate EG branch. The AU branch and the doubly degenerate EU branch generate the same quadratic equation, whose roots give the eigenvalues of the triply degenerate T_{1u} and T_{2u} core molecular orbitals. Note that the T_{1u} core molecular orbital has a positive eigenvalue unless $p > \sqrt{5}(1 - m)$. Thus, with most likely values of the edge weights m and p , the icosahedrally weighted K_{12} graph (fig. 3) has four positive eigenvalues, namely the A_g and triply degenerate T_{1u} orbitals, rather than only the single positive eigenvalue characteristic of the unweighted K_{12} graph. Note also that setting $m = 0$ and $p = 0$ gives the spectrum of the icosahedron ($+5$, $+\sqrt{5}$ three times, -1 five times, $-\sqrt{5}$ three times), whereas setting $m = 1$ and $p = 1$ gives the spectrum of the K_{12} complete graph ($+11$, -1 eleven times).

This symmetry factoring procedure indicates that in the absence of core–surface and core–external orbital mixing, the energy parameters of the icosahedral core orbitals in $B_{12}H_{12}^{2-}$ relative to α are determined by the equations

$$E(A_{1g}) = (5 + 5m + p)\beta_c, \quad (11a)$$

$$E(T_{1u})_c = [\sqrt{5}(1 - m) - p]\beta_c, \quad (11b)$$

$$E(H_g)_c = (-1 - m + p)\beta_c, \quad (11c)$$

$$E(T_{2u}) = [-\sqrt{5}(1 - m) - p]\beta_c, \quad (11d)$$

where β_c is the core orbital energy unit, m is the ratio of the *meta* (nonadjacent, nonantipodal) to *ortho* (adjacent) interactions, and p is the ratio of *para* (antipodal) to *ortho* interactions. The only core icosahedral orbitals not subject to core-surface mixing are the A_g principal core orbitals and the triply degenerate T_{2u} antibonding core orbitals. This leaves only the two eqs. (11a) and (11d) for the energy parameters of the A_g and T_{2u} core orbitals, respectively, to determine the three unknowns m , p , and β_c . The system is therefore underdetermined by one relationship so that an additional relationship between m , p , and/or β_c must be assumed before the necessary parameters can be extracted from the computed energy parameters. The arbitrary auxiliary assumption [19]

$$m = 2p \quad (12)$$

is therefore introduced, allowing the following two equations for β_c and m to be derived from eqs. (11a), (11d), and (12):

$$\beta_c = \frac{E(A_{1g})_c - (3.168)E(T_{2u})_c}{12.083}, \quad (13a)$$

$$m = 2p = \frac{2}{11} \left(\frac{E(A_{1g})_c}{\beta_c} - 5 \right). \quad (13b)$$

Analysis of the $3n$ computations by Hoffmann and Lipscomb [18] suggests that the values of m and β_c obtained from a given set of computed molecular orbital energy parameters are relatively insensitive to the assumed relationship between m and p in the range $0 < p < m$. After determining m and β_c by eqs. (13a) and (13b), eqs. (11b) and (11c) can be used to calculate hypothetical values for $E(T_{1u})_c$ and $E(H_g)_c$ in the absence of core-surface mixing. Comparison of these values with the computed energy parameters for the T_{1u} and H_g core orbitals gives parameters $\Delta E(T_u)$ and $\Delta E(H_g)$ measuring the extent of core-surface mixing.

An approach similar to that used for the octahedral $B_6H_6^{2-}$ can be used to estimate the surface orbital energy unit β_s for the icosahedral $B_{12}H_{12}$ corresponding to a given set of computed molecular orbital energy parameters. The ideal surface orbital energy parameters for the icosahedron based on S_{12} symmetry are determined by the equations

$$E(G_u) = E(H_g)_s = E(T_{1u})_s = \beta_s, \quad (14a)$$

$$E(G_g) = E(H_u) = E(T_{1g}) = -\beta_s. \quad (14b)$$

Reduction of the effective symmetry from the S_{12} automorphism group of the K_{12} graph to the actual I_h point group of the regular icosahedron destroys the equalities between the molecular orbital energy parameters in eqs. (14a) and (14b). On the basis of these equations, the following degeneracy weighted mean of the energy parameters of the pure bonding surface orbital G_u of degeneracy 4 and the pure antibonding surface orbitals G_g , H_u , and T_{1g} of degeneracies 4, 5, and 3, respectively, can be used to determine β_s :

$$\beta_s = 1/2[-1/12(4E(G_g) + 5E(H_u) + 3E(T_{1g})) + E(G_u)]. \quad (15)$$

As in the case of the analogous calculation for the $B_6H_6^{2-}$ octahedron, the energy parameters $E(H_g)_s$ and $E(T_{1u})_s$ are not included in the mean owing to uncertainties in estimating the core-surface mixing corrections $\Delta E(H_g)$ and $\Delta E(T_{1u})$.

These methods have been used to analyze the molecular orbital energy parameters arising from several different types of computations on octahedral $B_6H_6^{2-}$ (table 1) and icosahedral $B_{12}H_{12}^{2-}$ (table 2). The simplest such computations are the Hoffmann-Lipscomb LCAO-MO extended Hückel computations, which have been performed using only the $3n$ internal orbitals on the n vertex boron atoms (HL3n), using only the $4n$ boron valence orbitals (HL4n), and using the full $5n$ valence orbital set consisting of 4 orbitals (sp^3) on each boron atom and the 1s orbital on each hydrogen atom. The molecular orbital energy parameters from these computations are given in dimensionless quantities $(\alpha - E_k)/(K - E_k)$, where K is the proportionality constant between resonance integral β and overlap S : $\beta_{rs} = KS_{rs}$. Comparison of these three sets of computations allows the examination of the effects of core-external orbital mixing since the external and hydrogen orbitals are deleted completely from the HL3n basis set. The Armstrong-Perkins-Stewart self-consistent field molecular orbital (SCFMO) computations (APS), which give molecular orbital energy parameters in electron volts, introduce iterative methods [42] and use numerical integration of the Slater orbitals of the standard type

$$\chi_\mu = N_\mu r_\mu^{n-1} \exp(-\alpha r_\mu/a_0) y_{l,m}(\theta_\mu, \phi_\mu). \quad (16)$$

The Gimarc-Dai SCF MO Gaussian 82 computations with an STO-3G basis set represent an example of a simple ab initio computation where the Slater orbitals (e.g. eq. (16)) are approximated by a sum of Gaussians of the form $\exp(-\alpha r^2)$ to facilitate evaluation of the necessary integrals [43]. The Gimarc-Dai computations give molecular orbital energy parameters in Hartrees. The values of α , β_c , β_c/β_s , B_s , t , and $\Delta E(T_{1u})$ obtained from the analysis of the molecular orbital energy parameters from these computations for octahedral $B_6H_6^{2-}$ are listed in table 1. Similarly, the values of

Table 1
Analysis of computations on octahedral $B_6H_6^{2-}$

	Hoffmann–Lipscomb extended Hückel computations			Armstrong–Perkins–Stewart self-consistent MO computations*	SCF MO ab initio Gaussian 82 computations*
	3n	4n	5n		
<i>Core orbitals</i>					
A_{1g}	2.969	3.066	3.210	-50.3	-1.126
T_{1u}	-0.829	-0.831	-0.844	13.8	0.596
(T_{1u} adjusted)	(-0.401)	(-0.434)	(-0.478)	(7.5)	(0.062)
E_g	-0.884	-0.887	-0.888	13.6	0.470
<i>Surface orbitals</i>					
T_{1u}	1.023	1.130	1.433	-26.1	-0.848
(T_{1u} adjusted)	(0.595)	(0.733)	(1.067)	(-18.6)	(-0.314)
T_{2g}	0.493	0.493	0.493	-11.1	-0.486
T_{2u}	-0.416	-0.416	-0.416	9.8	0.198
T_{1g}	-0.671	-0.671	-0.671	11.7	0.548
<i>Derived parameters</i>					
α	0	0	0	7.2	0.675
β_c	0.642	0.658	0.683	-10.7	-0.266
β_s	0.527	0.527	0.527	-8.1	-0.429
β_c/β_s	1.218	1.249	1.296	1.32	0.620
t	0.625	0.660	0.700	0.700	0.233
$\Delta E(T_{1u})$	0.428	0.397	0.366	-6.3	-0.534

*Relative to α as given.

α , β_c , β_c/β_s , β_s , m , $\Delta E(T_{1u})$ and $\Delta E(T_{1g})$ obtained for icosahedral $B_{12}H_{12}^{2-}$ are listed in table 2.

4. Conclusions

The information summarized in tables 1 and 2 indicates the following features of the various computations on octahedral $B_6H_6^{2-}$ and icosahedral $B_{12}H_{12}^{2-}$:

- (1) The Hoffmann–Lipscomb LCAO–MO extended Hückel computations (HL5n) [18] and the Armstrong–Perkins–Stewart self-consistent molecular orbital computations (APS) [20], both of which are derived directly from Slater-type orbitals, give very similar values of β_c/β_s and t , particularly in the case of octahedral $B_6H_6^{2-}$.

Table 2
Analysis of computations on icosahedral $B_{12}H_{12}^{2-}$

	Hoffmann–Lipscomb extended Hückel computations			Armstrong–Perkins–Stewart self-consistent MO computations*	SCF MO ab initio Gaussian 82 computations*
	3n	4n	5n		
<i>Core orbitals</i>					
A_{1g}	4.163	4.293	4.469	-70.6	-1.184
T_{1u}	-0.773	-0.827	-0.860	13.5	0.407
(T_{1u} adjusted)	(0.654)	(0.642)	(0.620)	(-8.8)	(-0.441)
H_g	-0.856	-0.862	-0.873	13.7	0.511
(H_g adjusted)	(-0.693)	(-0.711)	(-0.734)	(11.5)	(0.227)
T_{2u}	-0.886	-0.886	-0.887	13.1	0.459
<i>Surface orbitals</i>					
T_{1u}	1.907	1.990	2.370	-40.6	-0.998
(T_{1u} adjusted)	(0.480)	(0.521)	(0.890)	(-18.3)	(-0.150)
H_g	0.984	1.107	1.358	-21.7	-0.810
(H_g adjusted)	(0.815)	(0.956)	(1.219)	(-19.5)	(-0.526)
G_u	0.518	0.518	0.518	-4.7	-0.526
G_g	-0.471	-0.471	-0.471	9.6	0.156
H_u	-0.678	-0.678	-0.678	11.3	0.445
T_{1g}	-0.782	-0.782	-0.782	11.8	0.682
<i>Derived parameters</i>					
α	0	0	0	5.1	0.547
β_c	0.577	0.588	0.602	-9.3	-0.218
β_s	0.577	0.577	0.577	-7.8	-0.467
β_c/β_s	1.000	1.019	1.043	1.192	0.466
$m(=2p)$	0.402	0.418	0.441	0.471	0.078
p	0.201	0.209	0.220	0.235	0.039
$\Delta E(T_{1u})$	1.429	1.469	1.480	-22.3	-0.848
$\Delta E(H_g)$	0.163	0.151	0.139	-2.2	-0.284

*Relative to α as given.

- (2) The SCF MO ab initio Gaussian 82 computations (GD), which approximate Slater-type orbitals with a sum of Gaussians, give much lower values of both β_c/β_s and the nonadjacent core orbital interaction parameters (t for $B_6H_6^{2-}$ and m for $B_{12}H_{12}^{2-}$) than the HL5n and APS computations using Slater orbitals. This indicates that the representation of Slater-type orbitals by a sum of Gaussians, as is typical in modern ab initio computations, leads to significantly weaker apparent core bonding, approximated more closely by deltahedral (D_n) rather

than complete (K_n) topology, probably because Gaussian functions of the type $\exp(-\alpha r^2)$ fall off more rapidly at longer distances than Slater functions of the type $\exp(-\zeta r)$.

- (3) The T_{1u} orbitals which, if pure, would be non-bonding in octahedral (D_6) core topology for $B_6H_6^{2-}$ and bonding in icosahedral (D_{12}) core topology for $B_{12}H_{12}^{2-}$, become antibonding through strong core-surface mixing [17, 19, 21]. Because of this, the simpler graph-theory derived model [8–11], using complete core bonding topology where $G_c = K_n$, gives the correct numbers of bonding and antibonding orbitals even though the complete graph K_n is a poor approximation of the actual G_c corresponding to the computations using Gaussian orbitals.

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