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Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Relationship of Topological to Computational Methods for the Study of Chemical Bonding in Deltahedral Boranes

R. B. King

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Methods are described for separating the effects of core and surface bonding in computations of the molecular orbital energy parameters in the globally delocalized deltahedral boranes $B_nH_n^{2-}$ (n = 6, 7, 10, 12). This provides a basis for comparison of predictions from a simple graph-theory-derived model with Hoffmann–Lipscomb LCAO–MO extended Hückel computations and self-consistent molecular orbital computations of Armstrong, Perkins, and Stewart. In the octahedral $B_6H_6^{2-}$ the graph-theory-derived methods lead to the same numbers of skeletal bonding and antibonding orbitals as the computational methods, thereby confirming the inherent validity of simple graph-theory-derived methods in the treatment of the large variety of systems based on boron and/or metal octahedra. However, in the icosahedral $B_{12}H_{12}^{2-}$ the graph-theory-derived method leads to only one core-bonding orbital in contrast to the four core-bonding orbitals found in the computational methods after removal of the effects of core–surface mixing. However, core–surface mixing makes three of these originally four core-bonding orbitals antibonding so that the graph-theory-derived method gives the correct results despite this fundamental flaw. In the cases of the less symmetrical pentagonal-bipyramidal $B_7H_7^{2-}$ and 4,4-bicapped square-antiprismatic $B_{10}H_{10}^{2-}$, separating the effects of core and surface bonding leads to significant uncertainties. However, a reasonable method for treating these difficulties in the simplest computations on $B_{10}H_{10}^{2-}$ suggests essential agreement of the predictions of the graph-theory-derived method with the computational results. On the other hand, the case of $B_7H_7^{2-}$ resembles that of $B_{12}H_{12}^{2-}$ in that the graph-theory-derived method agrees with the computational results only after adjustments for core–surface mixing.

Introduction

In recent years methods based on graph theory have been shown to be very useful for the study of the chemical bonding topology in polyhedral boranes, carboranes, and metal clusters.[1-3] Subsequent work has shown this approach to be very effective in relating electron count to cluster shape for diverse boranes and metal clusters, using a minimum of computation. Systems treated explicitly by this approach include post-transition-element clusters,[4,5] osmium carbonyl clusters,[6] gold clusters,[7,8] platinum carbonyl clusters,[7,9] rhodium clusters having fused polyhedra,[10,11] and early-transition-metal halide clusters.[12,13] In addition, the chemical bonding topology as elucidated by such graph-theory-derived methods appears to relate to superconducting properties of infinitely extended systems as demonstrated by the application to such systems based on metal cluster structures, including the ternary molybdenum chalcogenides (Chevrel phases)[13,14] and ternary lanthanide rhodium borides.[13,15]

In view of the broad application of these graph-theory-derived methods for the study of chemical bonding topology in diverse systems, it is important to relate such methods to various computational approaches for the treatment of the same systems. An initial effort in this area was recently reported[16] that provided a comparison between graph-theoretical and extended Hückel methods for the study of chemical bonding in octahedral and icosahedral boranes. This paper both extends the scope of such comparisons and defines the limits of the ability to make such comparisons. In this connection such comparisons are restricted in this paper to boranes in order to avoid the considerable complication of the d orbitals in transition-metal systems, which, because of mixing effects, appears to make intractable any comparisons of the type discussed in this paper. Nevertheless, well-known isolobal analogies[17,18] between boranes and carboranes on the one hand and transition- and post-transition-metal clusters on the other hand justify the use of analogous chemical bonding models for all of these types of systems so that the general observations in this paper are relevant to the diverse types of systems treated by topological and graph-theoretical methods.

Topology and Hückel Theory

The chemical bonding topology can be represented by a graph in which the vertices correspond to atoms or orbitals participating in the bonding and the edges correspond to bonding relationships. The adjacency matrix[19] **A** of such a graph can be defined as follows:

$$\begin{aligned} A_{ij} &= 0 \text{ if } i = j \\ &= 1 \text{ if } i \text{ and } j \text{ are connected by an edge} \\ &= 0 \text{ if } i \text{ and } j \text{ are not connected by an edge} \end{aligned} \qquad (1)$$

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

$$|\mathbf{A} - x\mathbf{I}| = 0 \qquad (2)$$

where **I** is the unit matrix ($I_{ii} = 1$ and $I_{ij} = 0$ for $i \neq j$). These eigenvalues are closely related to the energy levels as determined by Hückel theory.[20-23] which uses the secular equation

$$|\mathbf{H} - E\mathbf{S}| = 0 \qquad (3)$$

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:

$$\mathbf{H} = \alpha\mathbf{I} + \beta\mathbf{A} \qquad (4a)$$

$$\mathbf{S} = \mathbf{I} + S\mathbf{A} \qquad (4b)$$

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Table I. Core and Surface Orbitals for Deltahedra Having Only Degree 4 and Degree 5 Vertices

deltahedron	symmetry point group	no.			core orbitals[a]	surface orbitals[a]
		vertices	edges	faces		
octahedron	O_h	6	12	8	$A_{1g}^* + T_{1u} + E_g^*$ (2)	$T_{1u} + T_{2g}^* + T_{2u}^* + T_{1g}^*$ (3)
pentagonal bipyramid	D_{5h}	7	15	10	$2A_1^* + E_1' + E_2' + A_2''$ (1)	$A_2' + 2E_1' + E_2' + A_2'' + 2E_1''^* + E_2''^*$ (3)
bisdisphenoid ("D_{2d} dodecahedron")	D_{2d}	8	18	12	$2A_1 + 2B_2 + 2E$ (0)	$2A_1 + 2A_2^* + 2B_1^* + 2B_2 + 4E$ (2)
4,4,4-tricapped trigonal prism	D_{3h}	9	21	14	$2A_1' + 2E' + A_2'' + E''$ (0)	$A_1' + 2A_2'^* + 3E' + A_1''^* + 2A_2'' + 3E''$ (2)
4,4-bicapped square antiprism	D_{4d}	10	24	16	$2A_1 + 2B_2 + E_1 + E_2 + E_3$ (0)	$A_1 + A_2^* + B_1^* + B_2 + 3E_1 + 2E_2 + 3E_3$ (2)
icosahedron	I_h	12	30	20	$A_g^* + T_{1u} + T_{2u}^* + H_g$ (2)	$T_{1u} + H_g + G_u^* + G_g^* + H_u^* + T_{1g}^*$ (4)

[a] "Pure" core and surface orbitals are starred, and the numbers of such orbitals for each deltahedron are given in parentheses.

The energy levels of the system are thus related to the eigenvalues, x, of the adjacency matrix **A** (eq 2) as follows:

$$E = \frac{\alpha + x\beta}{1 + xS} \tag{5}$$

In eq 5 the three parameters α, β, and S are needed to relate the eigenvalues x to the corresponding energies E. However, any actual system provides far too few relationships to determine fully all of these three parameters so that all actual systems are underdetermined. Therefore, some assumptions concerning the values of α, β, and S are necessary for any comparisons to be feasible. If such assumptions do not affect the signs of the energies E, then qualitative chemical inferences using these assumptions will be valid. A similar philosophy but different mathematics is involved in some qualitative approaches to energy-level distributions in planar systems recently developed by Sinanoğlu.[24,25]

The first simplifying assumption, and one which is alway made, is a zero value for the parameter S. This reduces eq 5 to the linear equation

$$E = \alpha + x\beta \tag{6}$$

and reduces from 3 to 2 the number of parameters needed to determine energy levels from the eigenvalues. This level of simplification is already sufficient for meaningful comparisons of this topological approach to computational approaches in octahedral and icosahedral boranes, provided that energies of *all* of the molecular orbitals, antibonding as well as bonding and nonbonding, are available. In Hückel theory the parameter α is also taken to be zero so that eq 6 reduces further to

$$E = x\beta \tag{7}$$

In this case the energy levels are directly proportional to the eigenvalues of the adjacency matrix. The previous paper[16] compared the graph-theory-derived approach only with the original Hoffmann–Lipscomb LCAO–MO extended Hückel computations[26,27] where $\alpha = 0$ and eq 7 can be used. This paper extends the sophistication of the computations with which the comparison of graph-theory-derived methods is made to computations where $\alpha \neq 0$ and eq 6 rather than eq 7 is used.

Globally Delocalized Deltahedra

The polyhedral boranes discussed in this paper exhibit globally delocalized bonding[1-3] and are based on deltahedra having only degree 4 and degree 5 vertices. In this context a deltahedron is defined as a polyhedron in which all faces are triangles and the degree of a vertex is the number of edges meeting at that vertex. The six deltahedra having only degree 4 and degree 5 vertices are depicted in Figure 1, and some of their properties are listed in Table I. A vertex boron atom in such deltahedral boranes uses three of its four valence orbitals for skeletal (intrapolyhedral) bonding, leaving one valence orbital as an external orbital to bond to the external group, typically a monovalent group such as hydrogen or halogen. A major achievement of the graph-theory-derived approach to the chemical bonding topology in 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.[1-3] In such systems the three internal orbitals on each vertex atom are partitioned into two twin internal orbitals (called tangential in some treatments[28]) and a unique internal orbital (called radial in some treatments[28]). 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 eq 4a, 5, 6, and 7. This portion of the chemical bonding topology can be represented by a disconnected graph having $2n$ vertices corresponding to the $2n$ twin internal orbitals and n K_2 components; a K_2 component has only two vertices joined by an edge. The dimensionality of this bonding of the twin internal orbitals is one less than the dimensionality of the globally delocalized system.[29] Thus, in the case of the two-dimensional planar polygonal systems such as benzene, 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[30] to the sphere.

The equal numbers of bonding and antibonding orbitals formed by pairwise overlap of the twin internal orbitals are supplemented

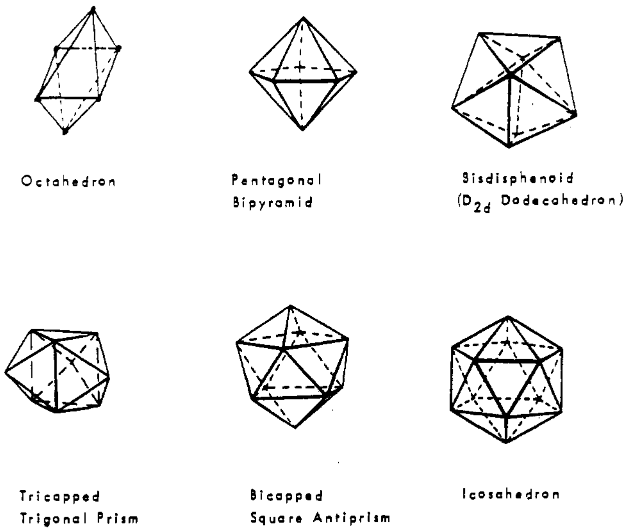

Figure 1. The six deltahedra having only degree 4 and degree 5 vertices listed in Table I.

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by additional bonding and antibonding molecular orbitals formed by global mutual overlap of the n unique internal orbitals. This bonding topology can be represented by a graph G 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. In the case of the deltahedral systems, graph G is *not* the graph of the actual deltahedron (more precisely, its 1-skeleton[31]) but instead the so-called complete graph K_n defined below. The relative energies of the additional molecular orbitals arising from such overlap of the unique internal orbitals are determined from the eigenvalues x of the adjacency matrix A of graph G by using β or, more specifically, β_c as the energy unit (eq 2–7). In the case of benzene graph G is the C_6 graph (the 1-skeleton of the hexagon) which has three positive and three negative eigenvalues corresponding to the three π-bonding and three π^*-antibonding orbitals, respectively. In the case of a globally delocalized deltahedron having n vertices, such as found in the deltahedral boranes $B_nH_n^{2-}$ and the carboranes $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$), graph G is the complete graph K_n in which each of the vertices has an edge going to every other vertex, leading to a total of $n(n-1)/2$ edges.[32] This corresponds to an n-center bond at the center (core) of the deltahedron formed by the overlap of each unique internal orbital with every other unique internal orbital. Regardless of the value of n, the complete graph K_n has only one positive eigenvalue, namely $n-1$, and $n-1$ negative eigenvalues, namely -1 each, indicating that the n-center core bond in a globally delocalized deltahedron leads to only one new bonding molecular orbital. The sum of the n bonding orbitals arising from the surface bonding of the twin internal orbitals and the single bonding orbital arising from the n-center core bonding of the unique internal orbitals gives a total of $n + 1$ bonding orbitals for globally delocalized deltahedra having n vertices. Filling these $n + 1$ bonding orbitals with electron pairs in the usual way gives a total of $2n + 2$ bonding electrons in accord with the experimentally observed number of skeletal electrons required to form stable globally delocalized deltahedral boranes and carboranes.

This graph-theory-derived approach to the chemical bonding topology of globally delocalized deltahedral boranes assumes that the symmetry of the skeletal bonding is the automorphism group of the K_n complete graph of the n-center core bonding, namely the symmetric group S_n having $n!$ operations,[33] rather than the lower symmetry of the actual deltahedron. Thus, consider the octahedral borane $B_6H_6^{2-}$. The corresponding complete graph K_6 has $(6)(5)/2 = 15$ edges and the S_6 automorphism group with $6! = 720$ operations. Among the 15 edges of K_6, 12 edges represent overlap of the unique internal orbitals located on adjacent vertex atoms of the octahedron, namely a pair of atoms connected by one of the 12 edges of the octahedron. Such edges represent cis interactions. The remaining $15 - 12 = 3$ edges of the K_6 graph represent overlap of the unique internal orbitals situated on one of the three pairs of antipodal vertices of the octahedron. Such edges represent trans interactions. Use of an unweighted K_6 graph to depict the core-bonding topology in an octahedron gives equal weights to the cis and trans interactions despite their obvious geometric difference. The actual maximum O_h rather than S_6 symmetry of octahedral systems will result in partial or complete lifting of the 5-fold degeneracy of the core-antibonding orbitals and the 6-fold degeneracies of the surface-bonding and surface-antibonding orbitals arising from application of the graph-theory-derived model outlined above. If in an octahedral system the magnitudes of the cis and trans interactions are taken to be unity and t, respectively, then the proximity of t to unity can be taken to represent the closeness of the approximation of the graph-theory-derived model to the actual chemical bonding topology of the system. However, the previous paper[16] showed that any *positive* value of t for an octahedral borane such as $B_6H_6^{2-}$ leads to the same number of skeletal bonding orbitals as predicted by the graph-theory-derived method where t is effectively taken to be unity.

Reduction of the symmetry from that of the symmetric groups S_n ($6 \leq n \leq 12$) to the symmetry group of the actual deltahedron not only splits some molecular orbitals of high degeneracies but also leads to some mixing of the core and surface bonding. For example, in the case of octahedral boranes under O_h symmetry, the core bonding has the representation $A_{1g} + T_{1u} + E_g$ and the surface bonding has the representation $T_{1u} + T_{2g} + T_{2u} + T_{1g}$. The T_{1u} core- and surface-bonding molecular orbitals can therefore overlap, leading to corresponding lowering and raising of the energies of these two molecular orbitals (designated as $\Delta E(T_{1u})$). Therefore, the T_{1u} orbital energies of octahedral boranes determined by computational methods based on O_h symmetry do not correspond to pure core or surface bonding but also include the interaction $\Delta E(T_{1u})$, which represents another variable that needs to be evaluated before the graph-theory-derived methods can be compared with various computations. Thus in an octahedral borane such as $B_6H_6^{2-}$ under O_h symmetry, only the A_{1g} and E_g molecular orbitals can represent pure core bonding and the T_{2g}, T_{2u}, and T_{1g} orbitals can represent pure surface bonding. Only these pure orbitals are useful for comparison of results from various computations with the simple predictions from the graph-theory-derived approach obtained as outlined above. Since the E_g pure core-bonding orbital and the T_{2u} and T_{1g} pure surface orbitals are all antibonding orbitals, only computations giving the energies of not only the filled bonding orbitals but also the empty antibonding orbitals (also called "virtual orbitals")[34] can meaningfully be compared with predictions from the graph-theory-derived method. This limitation severely restricts the range of comparisons that can be made since many important reported computations on deltahedral boranes[35–39] do not report all of the antibonding orbital energies necessary or such comparisons. If orbitals from the external bonding of the deltahedron are also included in the computation (e.g., the "4N" and "5N" computations of Hoffmann and Lipscomb[26,27]), then mixing between core and external orbitals is also possible. The previous paper[16] bypasses this potential difficulty by avoiding comparisons of such computations with results predicted by the graph-theory-derived method. This paper includes such comparisons of the 4N and 5N computations of Hoffmann and Lipscomb[26,27] as well as more modern 5N computations of Armstrong, Perkins, and Stewart.[40] The similarities of the energies of the core and surface orbitals in the 4N and 5N computations of Hoffmann and Lipscomb[26,27] to those in the 3N computations suggest that mixing between core and external orbitals belonging to the same irreducible representation is not large enough to prevent meaningful comparisons from being made. However, attempts to extend such comparisons to computations on octahedral transition-metal clusters (e.g., the computation on $Co_6(CO)_{14}^{4-}$ by Mingos[41]) appear to fail owing to strong mixing between transition-metal d orbitals and skeletal deltahedral orbitals belonging to the same irreducible representations.

Table I summarizes the core and surface orbitals of the six deltahedra having only degree 4 and degree 5 vertices. Among these deltahedra only the octahedron and icosahedron have as many as two pure core orbitals, the pentagonal bipyramid has only one pure core orbital, and the remaining three deltahedra have no pure core orbitals. For this reason, detailed comparisons between the results of computations and predictions from the

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graph-theory-derived method are feasible only for the octahedral and icosahedral boranes. However, even the less symmetrical deltahedra have at least two pure surface orbitals. If these include both bonding and antibonding orbitals, then both α and β_s can be estimated from their energies and the core orbital energies can be compared with β_s, assuming that $\beta_c \approx \beta_s$. Unfortunately, however, the two pure surface orbitals A_2 and B_1 of the 10-vertex 4,4-bicapped square antiprism, the lower symmetry deltahedron of Table I on which the most computations have been made, are both antibonding orbitals. For this reason, even the extremely limited comparison of computations that can be made for this system is only feasible for the original Hoffmann–Lipscomb computations[26,27] on $B_{10}H_{10}^{2-}$ where α can be taken to be zero and thus does not have to be determined from the computed energies.

Octahedral Boranes

Symmetry-factoring methods[42] described in greater detail in the previous paper[16] indicate that the energy parameters of the octahedral core orbitals in $B_6H_6^{2-}$ can be determined by the following equations, assuming that α is zero, β_c is the core orbital energy unit, and t is the ratio of trans to cis interactions:

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

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

$$E(E_g) = (-2 + t)\beta_c \tag{8c}$$

Since the A_{1g} and E_g orbitals are pure core orbitals, the two equations (8a) and (8c) can be used to calculate the values of the two parameters t and β_c corresponding to the $E(A_{1g})$ bonding and $E(E_g)$ antibonding energies obtained from a given computation, provided $\alpha = 0$ or is already known. Substitution of these calculated values for t and β_c in eq 8b then gives a hypothetical value for $E(T_{1u})_c$ in the absence of core–surface mixing. Comparison of this hypothetical value with the computed value for the T_{1u} *core* orbitals determines $\Delta E(T_{1u})$.

A related approach can then be used to compare the computed octahedral surface orbital energy parameters with the ideal values arising from the graph-theory-derived method. In this case the ideal surface orbital energy parameters are the following, with β_s designating the surface orbital energy unit:

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

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

Reduction of the effective symmetry from the S_6 automorphism group of the K_6 graph implied by the graph-theory-derived model 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 eq 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:

$$\beta_s = \tfrac{1}{2}[-\tfrac{1}{2}(E(T_{2u}) + E(T_{1g})) + E(T_{2g})] \tag{10}$$

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.

Table II summarizes the results that are obtained by applying these methods to the molecular orbital energy parameters computed by Hoffmann and Lipscomb[26] using the extended Hückel method where α may be taken to be zero. The value of t falls in the range 0.625–0.7, as compared with 1 for equal cis and trans unique internal orbital interactions in the six-center core bond required by the K_6 graph in the ideal graph-theory-derived method. The value β_c/β_s for the ratio of the core-bonding unit β_c to the surface-bonding unit β_s ranges from 1.2 to 1.3. However, some but not all of this discrepancy from unity can be attributed to the failure to include the low-energy but impure T_{1u} surface orbital in the weighted mean of eq 10. Also, as external orbitals become increasingly involved as one goes from the 3N to the 4N and then the 5N computations, the T_{1u} surface orbitals, even after the subtraction of $\Delta E(T_{1u})$, become much more bonding than the β_s predicted by eq 9a, apparently owing to mixing between the T_{1u} surface and T_{1u} external orbitals.

Table II. Molecular Orbital Energy Parameters for the Octahedral Borane $B_6H_6^{2-}$

	Hoffmann–Lipscomb extended Hückel computations			Armstrong–Perkins–Stewart self-consistent MO computations
	3N	4N	5N	
	Energy Parameters			
α	0	0	0	9.8
β_c	0.642	0.658	0.683	−10.7
β_s	0.527	0.527	0.527	−8.1
β_c/β_s	1.218	1.249	1.296	1.32
t	0.625	0.660	0.700	0.944
$\Delta E(T_{1u})$	0.428	0.397	0.366	−1.2
	Core Orbitals			
A_{1g}	2.969	3.066	3.210	−52.9
T_{1u}	−0.829	−0.831	−0.844	11.3
(T_{1u} adjusted)	(−0.401)	(−0.434)	(−0.478)	(10.1)
E_g	−0.884	−0.887	−0.888	11.5
	Surface Orbitals			
T_{1u}	1.023	1.130	1.433	−28.7
(T_{1u} adjusted)	(0.595)	(0.733)	(1.067)	−27.5
T_{2g}	0.493	0.493	0.493	−8.1
T_{2u}	−0.416	−0.416	−0.416	7.2
T_{1g}	−0.671	−0.671	−0.671	9.1
	External Orbitals (Bonding or Nonbonding)			
A_{1g}		0.204	0.951	−15.2
T_{1u}		−0.144	0.337	−12.5
E_g		−0.089	0.652	−16.1
	External Antibonding Orbitals			
A_g			−0.753	10.7
T_{1u}			−0.776	11.2
E_g			−0.803	11.0

A similar approach can be used to treat the molecular orbital energy parameters of $B_6H_6^{2-}$ computed by Armstrong, Perkins, and Stewart[40] using a self-consistent molecular orbital method including all valence electrons and the terminal hydrogen atoms (i.e., a 5N computation in the terminology of Hoffmann and Lipscomb[26,27]). In this case $\alpha \neq 0$ so that α must be determined from the computed orbital energy parameters before β_c and t can be calculated from eq 8a and 8c. Such a determination of α is best performed by taking the midpoint between the mean energy parameters of the two pure antibonding surface orbitals T_{2u} and T_{1g} and the energy parameter of the single pure bonding surface orbital T_{2g}, i.e.

$$\alpha = \tfrac{1}{2}[\tfrac{1}{2}(E(T_{2u}) + E(T_{1g})) + E(T_{2g})] \tag{11}$$

This equation for α is identical with eq 10 for β_s except for one change in sign. Again, the impure T_{1u} surface orbital is not included in the mean because of the uncertainty in the core–surface mixing parameter $\Delta E(T_{1u})$. The Armstrong–Perkins–Stewart energy parameters in Table II are given relative to α; i.e., the 9.8 value for α obtained from eq 11 has been subtracted from the molecular orbital energy parameters listed in Table I of the paper by Armstrong, Perkins, and Stewart[40] to give the parameters listed in Table II.

The most striking feature of the parameters given in Table II for the Armstrong–Perkins–Stewart computations is the closeness of such parameters to those predicted from the graph-theory-derived model. This is most dramatically revealed in the value for t of 0.944, which is very close to the ideal value of unity. Also the core–surface mixing of the T_{1u} orbitals is very small in these computations since $\Delta E(T_{1u})$ is only −1.2 or ~11% of the unadjusted energy parameter for the T_{1u} core orbital in contrast to the $\Delta E(T_{1u})$ of 0.366 or ~43% of the unadjusted energy parameter for the T_{1u} core orbital in the Hoffmann–Lipscomb 5N compu-

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[42] King, R. B. *Theor. Chim. Acta* **1977**, *44*, 223.

tations. The energy parameter of the bonding T_{1u} surface orbital even after adjustment by $-\Delta E(T_{1u})$ is much more strongly bonding ($\sim {}^7/_2\beta_s$) than the β_s value expected from the graph-theory-derived model apparently owing to strong mixing of this orbital with the external T_{1u} orbitals. The β_c/β_s value of 1.32 found for the Armstrong–Perkins–Stewart[40] computations is very close to the value of 1.296 found for the Hoffmann–Lipscomb computations.[26]

The general pattern of molecular orbital energy parameters for the octahedral borane $B_6H_6^{2-}$ (Table II) has the A_{1g} core-bonding orbital at much lower energies (more strongly bonding) than any other molecular orbital. A similar pattern of molecular orbital energy parameters is *not* found for the Wolfsberg–Helmholtz molecular orbital calculations by Mingos[41] on the octahedral transition-metal cluster $Co_6(CO)_{14}^{4-}$ in which the energy parameters for 31 molecular orbitals, including the A_{1g} core-bonding orbital, are clustered in a relatively narrow range (i.e., from −1.0857 to −0.9356 of the cobalt d-valence-orbital ionization energy). This suggests that $\beta_c \ll \beta_s$ for these calculations on $Co_6(CO)_{14}^{4-}$. Analysis of the calculated molecular orbital energy parameters[41] for $Co_6(CO)_{14}^{4-}$ similar to those summarized in Table II for $B_6H_6^{2-}$ appears unfeasible owing to uncertainties in the mixing of the cobalt d orbitals as well as the external orbitals with the Co_6 skeletal orbitals, which generates far too many undetermined parameters for the available number of relationships.

Icosahedral Boranes

The symmetry-factoring methods[42] described in detail in the previous paper[16] indicate that the energy parameters of the icosahedral core orbitals in $B_{12}H_{12}^{2-}$ can be determined by the following equations, assuming that α is zero, 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 the para (antipodal) to ortho interactions:

$$E(A_{1g}) = (5 + 5m + p)\beta_c \tag{12a}$$

$$E(T_{1u})_c = [5^{1/2}(1 - m) - p]\beta_c \tag{12b}$$

$$E(H_g)_c = (-1 - m + p)\beta_c \tag{12c}$$

$$E(T_{2u}) = [-5^{1/2}(1 - m) - p]\beta_c \tag{12d}$$

Since only the A_{1g} and T_{2u} orbitals are pure core orbitals, only the two equations (12a) and (12d) are available to calculate the values of the three parameters m, p, and β_c corresponding to the $E(A_{1g})$ bonding and $E(T_{2u})$ antibonding energy parameters obtained from a given computation provided that $\alpha = 0$ or is already known. This system is therefore underdetermined by one relationship. An additional relationship between the parameters m and p thus must be assumed before the necessary parameters can be extracted from the computed energy parameters. This paper arbitrarily makes the assumption

$$m = 2p \tag{13}$$

The analysis of the 3N computations of Hoffmann and Lipscomb[26] in the previous paper[16] suggests that this analysis is relatively insensitive to the assumed relation between m and p in the range $0 \leq p \leq m$. Equations 12a, 12d, and 13 are thus used to determine the values for the three parameters m, p, and β_c. Equations 12b and 12c can then be used to calculate hypothetical values for $E(T_{1u})_c$ and $E(H_g)_c$ in the absence of core–surface mixing. Comparisons of these values with the computed energy parameters for the T_{1u} and H_g *core* orbitals determined $\Delta E(T_{1u})$ and $\Delta E(H_g)$.

An approach similar to that used for the octahedral borane $B_6H_6^{2-}$ can be used to estimate the surface orbital energy unit β_s for $B_{12}H_{12}^{2-}$ corresponding to a given set of computed molecular orbital energy parameters. The ideal surface orbital energy parameters are related to this unit as follows:

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

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

Reduction of the effective symmetry from the S_{12} automorphism group of the K_{12} graph implied by the graph-theory-derived model to the actual I_h point group of a regular icosahedron will destroy the equalities between the molecular orbital energy parameters in eq 14a and 14b. On the basis of these equations the following appropriately weighted mean of the energy parameters of the pure bonding surface orbital G_u and the pure antibonding surface orbitals G_g, H_u, and T_{1g} can be used to determine β_s:

$$\beta_s = {}^1\!/_2[-{}^1\!/_3(E(G_g) + E(H_u) + E(T_{1g})) + E(G_u)] \tag{15}$$

Table III. Molecular Orbital Energy Parameters for the Icosahedral Borane $B_{12}H_{12}^{2-}$

	Hoffmann–Lipscomb extended Hückel computations			Armstrong–Perkins–Stewart self-consistent MO computations
	3N	4N	5N	
		Energy Parameters		
α	0	0	0	8.2
β_c	0.577	0.588	0.602	−8.9
β_s	0.580	0.580	0.580	−7.8
β_c/β_s	0.993	1.013	1.038	1.141
m (=2p)	0.403	0.418	0.441	0.597
p	0.201	0.209	0.220	0.298
$\Delta E(T_{1u})$	1.427	1.469	1.480	−15.9
$\Delta E(H_g)$	0.169	0.151	0.139	1.0
		Core Orbitals		
A_g	4.163	4.293	4.469	−73.7
T_{1u}	−0.773	−0.827	−0.860	10.4
(T_{1u} adjusted)	(0.654)	(0.642)	(0.620)	(−5.4)
H_g	−0.856	−0.862	−0.873	10.6
(H_g adjusted)	(−0.693)	(−0.711)	(−0.734)	(11.6)
T_{2u}	−0.886	−0.886	−0.887	10.5
		Surface Orbitals		
T_{1u}	1.907	1.990	2.370	−43.7
(T_{1u} adjusted)	(0.480)	(0.521)	(0.890)	−27.8)
H_g	0.984	1.107	1.358	−24.8
(H_g adjusted)	(0.815)	(0.956)	(1.219)	(−25.8)
G_u	0.518	0.518	0.518	−7.8
G_g	−0.471	−0.471	−0.417	6.5
H_u	−0.678	−0.678	−0.678	8.2
T_{1g}	−0.782	−0.782	−0.782	8.7
		External Orbitals (Bonding or Nonbonding)		
A_g		0.619	1.485	−24.0
T_{1u}		0.150	0.619	−13.7
H_g		−0.239	0.240	−9.5
T_{2u}		−0.225	0.460	−10.7
		External Antibonding Orbitals		
A_g			−0.718	9.7
T_{1u}			−0.690	8.1
H_g			−0.783	9.7
T_{2u}			−0.812	10.0

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 this mean owing to uncertainties in estimating the core–surface mixing corrections $\Delta E(H_g)$ and $\Delta E(T_{1u})$.

Table III summarizes the results that are obtained by applying these methods to the molecular orbital energy parameters of $B_{12}H_{12}^{2-}$ computed by Hoffmann and Lipscomb[26] using the extended Hückel method and those computed by Armstrong, Perkins, and Stewart[40] using a self-consistent molecular orbital method. In the former case α may be taken to be zero whereas in the latter case α is not zero but can be calculated from the following relationship by using the energy parameters of the G_u, G_g, H_u, and T_{1g} pure surface orbitals:

$$\alpha = {}^1\!/_2[{}^1\!/_3(E(G_g) + E(H_u) + E(T_{1g})) + E(G_u)] \tag{16}$$

The values for the parameters m and p ($m \approx 0.4$ for the Hoffmann–Lipscomb computations and $m \approx 0.6$ for the Armstrong–Perkins–Stewart computations) are found to deviate further from the ideal value of unity expected from the graph-theory-derived method than the related parameter t for octahedral $B_6H_6^{2-}$ (Table II) from the corresponding computations. This is in accord with the larger size of the icosahedron relative to that of the octahedron, which can generate greater differences between the core overlap of unique internal orbitals from adjacent vertex atoms and those from nonadjacent vertex atoms. In the icosahedral system the value of m (and thus that of p) is closer to unity for the Armstrong–Perkins–Stewart computation[40] than that for the Hoffmann–Lipscomb computation[26] (Table III), as was found in the octahedral system for the related parameter t. For the Hoffmann–Lipscomb computation (Table III) and to a lesser extent (~14% error) also for the Armstrong–Perkins–Stewart computations, the approximation $\beta_c \approx \beta_s$ (i.e., $\beta_c/\beta_s \approx 1$) appears valid; an approximation of this type is useful for the treatment of less symmetrical and thus highly underdetermined deltahedra.

By far, the most significant conclusion from the data in Table III is that the core bonding in icosahedral $B_{12}H_{12}^{2-}$ in the absence of core–surface mixing generates *four* core-bonding orbitals (A_{1g} + T_{1u}) rather than the single bonding orbital (A_{1g}) obtained by using the K_{12} complete graph to model the core-bonding topology. In this sense the graph-theory-derived model[1-3] is incorrect for the icosahedron. Nevertheless, the graph-theory-derived model works for icosahedral boranes and carboranes because this fundamental error is compensated by the T_{1u} core–surface mixing. The corresponding mixing energy, $\Delta E(T_{1u})$, is so large that the core T_{1u} orbitals are raised to antibonding energies by the core–surface interaction so that only one core-bonding orbital, namely the A_g orbital, remains after this interaction. This is why the graph-theory-derived model for icosahedral $B_{12}H_{12}^{2-}$ leads to the experimentally observed skeletal electron count even though the assumption of the K_{12} complete graph for the core-bonding topology leads to the incorrect number of core-bonding orbitals before core–surface mixing.

The chemistry of gold clusters[43,44] provides an important experimental test of these ideas. Many such clusters, which can be called[45] "porcupine compounds", consist of a central gold atom (the "body" of the porcupine) surrounded by a number of peripheral gold atoms (the "quills" of the porcupine). The p orbitals of the peripheral gold atoms have energies too high to function as twin internal orbitals for surface bonding,[46] an apparent consequence of relativistic effects[47] in the chemical bonding of the relatively heavy gold atom. Thus, the peripheral gold atoms in porcupine compounds form polyhedral clusters exhibiting core bonding (with the central gold as an interstitial atom) but no surface bonding.[7,8] Turning off the surface bonding in this way in the centered icosahedral $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$ [48] leads to four core-bonding orbitals,[7,8] as is found for $B_{12}H_{12}^{2-}$ when the effects of core–surface mixing are removed (Table III). This point may also relate to the general observation[7,8] that the overall topology of the $n - 1$ peripheral gold atoms in a centered Au_n porcupine cluster leads to electron counts corresponding not to those expected for a K_{n-1} complete graph but instead to that of the polyhedron formed by the peripheral gold atoms.

Less Symmetrical Deltahedral Boranes

Attempts to extend the methods outlined above to deltahedra that are less symmetrical than the octahedron or icosahedron lead to a number of immediate difficulties. Among the deltahedra listed in Table I other than the octahedron and icosahedron, the pentagonal bipyramid has only one pure core orbital and the remaining three deltahedra have no pure core orbitals. Thus, pure core orbital energy parameters are not available for the calculation of the energy unit β_c. In addition, the lower symmetries of these deltahedra lead to a much larger number of independent interaction parameters[48] between pairs of unique internal orbitals analogous to t for the octahedron and m and p for the icosahedron used above.

Table IV. Molecular Orbital Energy Parameters from the Hoffmann–Lipscomb "3N" Extended Hückel Computations for $B_7H_7^{2-}$

	computed by Hoffmann and Lipscomb	core–surface interaction	adjusted by removal of core–surface interaction
		Energy Parameters	
α	−0.032 (≈0)		
β_s (≈β_c)	+0.556		
		Surface Orbitals	
A_2'	−0.726	(weighted average used to determine β_s (≈β_c))	−0.556
$E_1''(1)$	+0.524		+0.556
$E_1''(2)$	−0.669		−0.556
E_2''	−0.371		−0.556
A_2''	+0.740	$\Delta E(A_2'') = -0.184$	+0.556
E_2'	+0.494	$\Delta E(E_2') = +0.062$	+0.556
$E_1'(1)$	+1.420	$\Delta E(E_1')_1 = -0.864$	+0.556
$E_1'(2)$	−0.508	$\Delta E(E_1')_2 = -0.048$	−0.556
		Core Orbitals	
$A_1'(1)$	+3.273	(pure core orbitals)	+3.273
$A_1'(2)$	−0.847		−0.847
E_1'	−0.840	$-\sum\Delta E(E_1')_n = +0.912$	+0.072
A_2''	−0.851	$-\Delta E(A_2'') = +0.184$	−0.667
E_2'	−0.845	$-\Delta E(E_2') = -0.062$	−0.907

The best approach for obtaining useful information from the molecular orbital energy parameters appears to be the following sequence of steps:

(1) Use standard group-theoretical methods[49] to find the core and surface orbital irreducible representations.

(2) Calculate the surface orbital energy unit β_s from the energies of the pure surface orbitals by using equations analogous to eq 10 and 15. If some of the pure surface orbitals are bonding and others antibonding, α for systems where $\alpha \neq 0$ can also be calculated by using equations analogous to eq 11 and 16, but such is not generally possible. If the pure surface orbitals are either all bonding or all antibonding, then only β_s can be calculated and comparison is limited to computations where α is known by other methods such as in the computations of Hoffmann and Lipscomb,[26,27] where α is taken to be zero. Such is the case for the 4,4-bicapped square antiprism, where both of the pure surface orbitals, namely A_2 and B_1, are antibonding.

(3) Estimate the other surface orbital energy parameters in the absence of core–surface mixing as β_s (bonding) or $-\beta_s$ (antibonding) by making assignments so that the total numbers of surface bonding and surface antibonding orbitals are equal, remembering to include in the counts the pure surface orbitals used above and to allow for degeneracies. Comparison of these estimated energy parameters with the computed energy parameters allows estimation of the core–surface mixing parameters ΔE. Several different partitions of the surface orbitals into equal numbers of bonding and antibonding orbitals may be possible.

(4) Assume $\beta_c \approx \beta_s$, which is a reasonable assumption in light of the comparisons of β_c and β_s independently obtained from the icosahedral $B_{12}H_{12}^{2-}$ computations (i.e., $\beta_c/\beta_s \approx 1$).

(5) Remove the effects of core–surface mixing from the core orbital energy parameters by subtracting $\sum\Delta E$ obtained for all surface orbitals belonging to the same irreducible representation.

(6) Express these core orbital energy parameters in terms of β_c (≈β_s).

(7) Compare the core orbital energy parameter coefficients of β_c with the corresponding eigenvalues of the spectrum of the graph corresponding to the interactions of interest, thereby applying eq 6 or 7. If both sets of numbers are close, then the assignments of surface orbitals as bonding or antibonding are probably correct. Otherwise, other assignments must be considered.

Tables IV and V illustrate this procedure for the most favorable cases, namely the Hoffmann–Lipscomb 3N computations[26,27] on $B_7H_7^{2-}$ and $B_{10}H_{10}^{2-}$, respectively, wherre α may be taken to be

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Table V. Molecular Orbital Energy Parameters from the Hoffmann–Lipscomb "3N" Extended Hückel Computations for $B_{10}H_{10}^{2-}$

	computed by Hoffmann and Lipscomb	core–surface interaction	adjusted by removal of core–surface interaction
		Energy Parameters	
α	0		
β_s ($\approx\beta_c$)	+0.665		
		Surface Orbitals	
A_2	−0.739	(averaged to give $-\beta_s$ ($\approx-\beta_c$))	−0.665
B_1	−0.590		−0.665
A_1	+1.004	$\Delta E(A_1) = -0.339$	+0.665
B_2	+1.978	$\Delta E(B_2) = -1.313$	+0.665
$E_1(1)$	+1.447	$\Delta E(E_1)_1 = -0.782$	+0.665
$E_1(2)$	+0.328	$\Delta E(E_1)_2 = +0.337$	+0.665
$E_1(3)$	−0.615	$\Delta E(E_1)_3 = -0.050$	−0.665
$E_2(1)$	+0.756	$\Delta E(E_2)_1 = -0.091$	+0.665
$E_2(2)$	−0.598	$\Delta E(E_2)_2 = -0.067$	−0.665
$E_3(1)$	+0.760	$\Delta E(E_3)_1 = -0.095$	+0.665
$E_3(2)$	−0.327	$\Delta E(E_3)_2 = -0.338$	−0.665
$E_3(3)$	−0.747	$\Delta E(E_3)_3 = +0.082$	−0.665
		Core Orbitals	
$A_1(1)$	+3.877	assumed 0	+3.877
$A_1(2)$	−0.812	$-\Delta E(A_1) = +0.339$	−0.473
$B_2(1)$	−0.812	$-^1/_2\Delta E(B_2) = +0.656$	−0.156
$B_2(2)$	−0.850	$-^1/_2\Delta E(B_2) = +0.655$	−0.195
E_1	−0.776	$-\sum\Delta E(E_1)_n = +0.495$	−0.281
E_2	−0.884	$-\sum\Delta E(E_2)_n = +0.158$	−0.726
E_3	−0.862	$-\sum\Delta E(E_3)_n = +0.351$	−0.511

zero and effects of mixing with external orbitals may be ignored. Elementary group-theoretical methods[49] (Table I) show that for $B_7H_7^{2-}$ the pure surface orbitals are $A_2' + 2E_1'' + E_2''$ and for $B_{10}H_{10}^{2-}$ the pure surface orbitals are $A_2 + B_1$. In the case of the $B_7H_7^{2-}$ pure surface orbitals, the A_2', the E_2'', and one of the E_1'' orbitals are antibonding whereas the other E_1'' orbital is bonding. The following weighted averages can be used to determine β_s and α:

$$\beta_s = \tfrac{1}{2}[-\tfrac{1}{3}(E(A_2') + E(E_1'')_2 + E(E_2'')) + E(E_1'')_1] = +0.556 \quad (17a)$$

$$\alpha = \tfrac{1}{2}[\tfrac{1}{3}(E(A_2') + E(E_1'')_2 + E(E_2'')) + E(E_1'')_1] = -0.032 \approx 0 \quad (17b)$$

Note that the value of α found by this method (−0.032) is close to the assumed value of zero. In the case of $B_{10}H_{10}^{2-}$ pure surface orbitals, both the A_2 and B_1 orbitals are antibonding (Table V) so that the parameter α cannot be determined from these data but must be assumed to be zero. Removal of the core–surface interaction for the remaining surface orbitals must lead to either β_s for the bonding orbitals or $-\beta_s$ for the antibonding orbitals, with assignments of bonding and antibonding character being made to give n bonding and n antibonding orbitals for $B_nH_n^{2-}$ (n = 7, 10). This allows determination of the ΔE parameters describing the magnitudes of the core–surface interactions. The negatives of these core–surface interaction parameters are added to the core orbital energy parameters obtained from the Hoffmann–Lipscomb computations[26,27] to give hypothetical core orbital energy parameters in the absence of core–surface mixing.

Table IV summarizes the results of this procedure for the pentagonal-bipyramidal $B_7H_7^{2-}$. The expected strong bonding $A_1'(1)$ orbital is found with a strongly positive energy parameter. In addition the degenerate E_1' core orbitals have slightly positive adjusted energy parameters whereas the remaining core orbitals ($A_1'(2)$, A_2'', and E_2') are clearly antibonding. Thus core–surface mixing appears necessary for the pentagonal-bipyramidal $B_7H_7^{2-}$ to give the single bonding and six antibonding core orbitals predicted by the graph-theory-derived method, analogous to the observations on the icosahedral $B_{12}H_{12}^{2-}$ system summarized above. This common feature of these two deltahedral systems may related in some way to the presence of a C_5 axis.

Table V summarizes the results of this procedure for the 4,4-bicapped square-antiprismatic $B_{10}H_{10}^{2-}$. In this case only one of the ten adjusted core orbital energy parameters, namely that of the $A_1(1)$ orbital, is strongly positive whereas the other nine parameters, namely those of the $A_1(2)$, $B_2(1)$, $B_2(2)$, and the three degenerate pairs E_1, E_2, and E_3, are weakly negative, in crude agreement with the spectrum of the K_{10} complete graph (one +9 eigenvalue and nine −1 eigenvalues) used in the graph-theory-derived model for the core overlap of the ten unique internal orbitals in this system.

Note, however, that in order to obtain the adjusted core orbital energy parameters in Table V, the core–surface interaction correction $\Delta E(A_1)$ is applied exclusively to the antibonding core orbital $A_1(2)$ whereas the core–surface interaction correction $\Delta E(B_2)$ is distributed equally between the two core orbitals $B_2(1)$ and $B_2(2)$. This apparently arbitrary procedure is justified on the basis that the strongly bonding fully symmetric $A_1(1)$ core orbital lies at such a low energy (i.e., a highly *positive* energy parameter) that it does not mix significantly with the A_1 surface orbital.

Summary

This paper describes methods for separating the effects of core and surface bonding in computations of the molecular orbital energy parameters in the globally delocalized deltahedral boranes $B_nH_n^{2-}$ (n = 6, 7, 10, 12). This provides a basis for comparison of the results from these computations with those predicted by simple graph-theory-derived methods.

The general conclusions from this comparison can be summarized as follows:

(1) $B_6H_6^{2-}$ (octahedron): The graph-theory-derived methods lead to the same numbers of skeletal bonding and antibonding orbitals as the computational methods, thereby confirming the inherent validity of simple graph-theory-derived methods in the treatment of the large variety of systems based on boron and/or metal octahedra.

(2) $B_{12}H_{12}^{2-}$ (icosahedron): The graph-theory-derived method leads to only one core-bonding orbital for the icosahedron in contrast to the four core-bonding orbitals found in the computational methods after removal of the effects of core–surface mixing. However, core–surface mixing makes three of these originally four core-bonding orbitals antibonding so that the graph-theory-derived method gives the correct results despite this fundamental flaw.

(3) $B_7H_7^{2-}$ (pentagonal bipyramid) and $B_{10}H_{10}^{2-}$ (4,4-bicapped square antiprism): Because of a limited number of pure core and pure surface orbitals for deltahedra of lower symmetry than the octahedron and icosahedron, separating the effects of core and surface bonding leads to significant uncertainties. However, a reasonable method for treating these difficulties in the simplest computations on $B_{10}H_{10}^{2-}$ suggests essential agreement of the computational results with those predicted by graph-theory-derived methods. However, in the case of $B_7H_7^{2-}$, as in the case of $B_{12}H_{12}^{2-}$, the effects of core–surface mixing appear to be necessary for the computational results to agree with expectations from the graph-theory-derived methods.

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Registry No. $B_6H_6^{2-}$, 12429-97-9; $B_7H_7^{2-}$, 12430-07-8; $B_{10}H_{10}^{2-}$, 12356-12-6; $B_{12}H_{12}^{2-}$, 12356-13-7.