3-Dimensional Hückel Theory for Cluster Compounds

Ming Zhao and B. M. Gimarc*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received March 23, 1993[⊗]

Applications of Hückel molecular orbital theory to planar aromatic hydrocarbons have been of enormous conceptual value to organic chemistry. The success of 2-dimensional Hückel theory is mainly a result of molecular connectivity or topology. But most of chemistry is 3-dimensional. In the widely applied 3-dimensional extended Hückel method, much of the significance of topology is lost or at least obscured in choices of bond distances, Coulomb integrals, and calibration parameters. We present a 3-dimensional version of Hückel theory developed directly from the approximations of simple Hückel theory plus a few additional assumptions. The significance of molecular topology is retained. The 3-dimensional Hückel theory we describe is designed specifically for polyhedral molecular clusters. Following an exposition of the method, we present applications to specific classes of clusters for which results can be compared with those from experiment and from *ab initio* molecular orbital calculations. For the *closo*-boranes, $B_nH_n^{2-}$, the 3-dimensional Hückel model correctly chooses experimentally observed structures from a large set of plausible polyhedral structures. The results also confirm the well-known rule of $n + 1$ skeletal electron pairs in the *closo*-boranes. For a group of transition metal clusters, the model provides a rationalization for the empirically observed numbers of cluster bonding electrons.

Introduction

Simple Hückel theory of 2-dimensional or planar molecular systems has been of enormous conceptual value in organic chemistry.[1,2] Compared to the large number of planar conjugated organic examples, planar inorganic molecules and ions are relatively few, but even these have been studied to conceptual advantage with simple Hückel methods.[3–5]

Applications of simple molecular orbital theory to three-dimensional structures have been widely done at the extended Hückel level.[6,7] Although extended Hückel theory is sometimes referred to as 3-dimensional Hückel theory,[8] this model differs from simple 2-dimensional Hückel theory by much more than an additional spatial dimension. The input for a 2-dimensional Hückel calculation could hardly be simpler: the number of atoms, the number of π electrons, and an adjacency matrix. The number of atoms counts the number of atomic orbitals in the basis set and thereby establishes the number of molecular orbitals for the system. The number of π electrons is the number of electrons delocalized over the planar, 2-dimensional structure in MOs that are antisymmetric with respect to reflection in the molecular plane. The adjacency matrix specifies whether or not we have drawn a bond between each pair of constituent atoms. Each element in the matrix is either unity, if a bond is present between two indexed atoms, or zero, if no bond is present. Thus, the adjacency matrix contains information about molecular connectivity or topology. This realization has been the basis for a brilliant reformulation of 2-dimensional Hückel theory in terms of graph theory.[9,10] Hydrogen atoms and other substituents are completely ignored. Coulomb and resonance integrals α and β, which are developed in the theoretical framework, do not appear in the calculations, at least for hydrocarbons. Heteroatoms can be included by specifying changes from still unspecified values of hydrocarbon Coulomb and resonance integrals, but their significance is mainly in the sign and relative size of those variations and not in the actual values chosen. Atomic orbital overlaps are completely neglected.

The extended Hückel input information is quite different. Instead of giving only connectivity information through an adjacency matrix, one must specify actual distances between atoms, usually by Cartesian coordinates of atomic positions. Coulomb integrals are given the values of atomic valence state ionization potentials, and these quantities are averaged and combined with distance-dependent overlap integrals to calculate resonance integrals between all pairs of atomic orbitals. Coulomb, resonance, and overlap integrals are all directly involved in the calculation. Hydrogen atoms and other substituents are routinely included. The results of extended Hückel calculations are expressed in conventional energy units, which have the unfortunate effect of lending the results undue quantitative significance.

The fact that the extended Hückel method does not include specific assignments of bond locations might be considered as an advantage. In practice, it is also a limitation. Total energies turn out to be rather sensitive to actual choices of interatomic distances, and while this leads to the possibility of determining structures by varying interatomic distances to minimize the total energy, molecular structures determined through geometry optimization by extended Hückel calculations are frequently disappointing and occasionally even molecular shapes and relative energies turn out to be wrong. As an alternative, standard bond distances and angles are sometimes used as input parameters for comparisons through series of related molecules,[7] but again the actual values of structural parameters chosen are open to criticism.

Qualitative models of the electronic structures of clusters have received considerable attention in recent years and several excellent reviews are available. Therefore, we mention in the

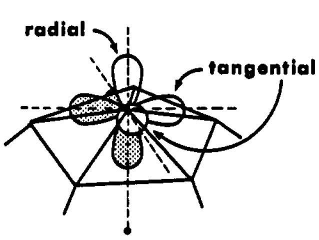
⊗ Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.
(2) Coulson, C. A.; O'Leary, B.; Mallion, R. B. *Hückel Theory for Organic Chemists*; Academic Press, New York, 1978.
(3) Gimarc, B. M.; Trinajstic, N. *Pure Appl. Chem.* **1980**, *52*, 1442; *Inorg. Chem.* **1982**, *21*, 21.
(4) Gimarc, B. M. *Croat. Chem. Acta* **1984**, *57*, 955.
(5) Gimarc, B. M.; Juric, A.; Trinajstic, N. *Inorg. Chim. Acta* **1985**, *102*, 105.
(6) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(7) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489.
(8) Sinanoglu, O.; Wiberg, K. B. *Sigma Molecular Orbital Theory*; Yale University Press: New Haven, CT, 1970.
(9) Graovac, A.; Gutman, I.; Trinajstic, N. *Topological Approach to the Chemistry of Conjugated Molecules*; Springer-Verlag: Berlin, 1977.
(10) Trinajstic, N. *Chemical Graph Theory*; CRC Press: Boca Raton, FL, 1983.
(11) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29.
(12) Mingos, D. M. P.; Zhenyang, L. *Struct. Bonding* **1989**, *71*, 1.

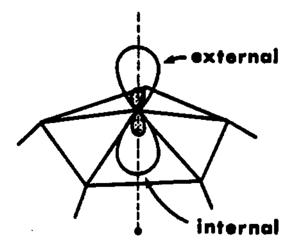
0020-1669/93/1332-4700$04.00/0

following only those models that provided the clearest inspiration for development of the model that we present here. In 1971, Wade formulated electron-counting rules for polyhedral clusters.[13] These rules specify that an n-atom closed polyhedron contains $n + 1$ pairs of delocalized electrons that account for bonding among the atoms that compose the framework or skeleton of the polyhedron. The $n + 1$ pairs are often referred to as skeletal electron pairs.

In 1977, King and Rouvray introduced a graph-theoretical model, based on a simple Hückel analysis, for the interpretation of bonding in polyhedral boranes, carboranes, and metal clusters.[14] Consider a structure in which n atoms or vertices are connected to form a polyhedron. Each atom contributes four valence AOs, one s and three p AOs, to the basis set for a total of $4n$ AOs. Imagine one of the p AOs at each vertex oriented such that it points along an axis running toward the center of the polyhedron. Call this the *radial AO*. The other two p AOs are perpendicular to this axis and are tangential to the surface of an imaginary sphere that encloses the polyhedron. Call these the *tangential AOs* (**1**). By combining the s AO and the radial p AO, one can



1



2

form two sp hybrid orbitals: an *internal hybrid* that points toward the center of the polyhedron and an *external hybrid* that points away from the polyhedral surface (**2**). The external hybrids can be used to form normal two-electron bonds to ligands or to hold unshared electron pairs. Since the n external hybrids are now engaged in localized, external bonding or as lone pairs, they need no longer be considered. Therefore, the total number of AOs available to describe polyhedral bonding reduces from $4n$ to $3n$.

If we assume no interactions between the set of n internal hybrids and the set of $2n$ tangential p AOs, the $3n \times 3n$ adjacency matrix breaks down into an $n \times n$ matrix for the internal hybrids and a $2n \times 2n$ matrix for the tangential orbitals. King and Rouvray assumed that the n internal hybrids are all neighbors or that they all combine or interact with each other with equal weight regardless of their location relative to one another in the polyhedron. This, of course, is not true for sp hybrids as we know them, but the assumption leads to a great simplification. The adjacency matrix specifying equal interactions among the internal hybrids will have 0's on the main diagonal and 1's elsewhere. This is the adjacency matrix for the *complete graph*, K_n, the eigenvalues of which are well-known. They include a single bonding MO with energy $-(n-1)\beta$ and $n - 1$ degenerate antibonding MOs, each with energy $+\beta$. The energies of these n MOs sum to zero:

$$\underbrace{-(n-1)\beta}_{\text{bonding}} + \underbrace{(n-1)(\beta)}_{\text{antibonding}} = 0$$

The unique bonding MO is called the *bonding core orbital*. Among the remaining $2n$ MOs made from combinations of the $2n$ tangential p AOs, half or n will be bonding and half will be antibonding. Therefore, the total number of bonding MOs is $n + 1$. This result of King and Rouvray is widely regarded as the first theoretical justification of the empirical observation that stable polyhedral boranes and carboranes are those that possess $n + 1$ pairs of skeletal electrons.

(13) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792; *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
(14) King, R. B.; Rouvray, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 7834.

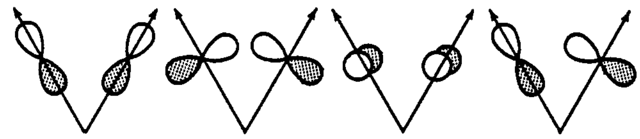


Figure 1. Orientations of orbitals in standard integrals. The orbitals p_x and p_y are tangential orbitals. The radial orbital is represented here as p_z.

As described above, the internal orbitals are sp hybrids that point toward the center of the polyhedron and are therefore functionally different from the unhybridized p AOs that make up the set of tangential AOs. In any 3-dimensional Hückel calculations that might actually be carried out, the functional forms are never used. For convenience in our development that follows, we represent the internal hybrids as unhybridized p AOs. But we might wish to recognize the difference between internal radial and tangential orbitals by attributing to them different Coulomb integrals.

Another elegant qualititative description of bonding in polyhedral clusters has been developed by Stone, whose tensor surface harmonic theory derives skeletal molecular orbitals as expansions of vector surface harmonic functions.[15] This theory is based on the free-electron model derived from the quantum-mechanical problem of a particle on the surface of a sphere. Stone was also able to give theoretical justification for the electron count of $n + 1$ skeletal electron pairs in stable polyhedral molecules. However, it should be mentioned that the count of $n + 1$ skeletal electron pairs depends largely on the interaction between radial and tangential orbitals. If this interaction is neglected, Stone's theory gives a result that the number of bonding orbitals is larger than $n + 1$ for $n \geq 9$. Other treatments have had the same problem of additional bonding orbitals when radial–tangential interaction is not considered. Fowler and Porterfield have developed an extended tensor surface harmonic theory to avoid incorrect orbital degeneracies in Stone's tensor surface harmonic theory.[16] Their use of the one-electron Hamiltonian and explicit calculation of radial–tangential interaction confirmed the qualitative conclusions of Stone.

3-Dimensional Hückel Theory for Clusters

A 3-dimensional Hückel theory for polyhedral clusters can be developed from the usual Hückel approximations and some additional assumptions.

A. Polyhedral Orientation and Basis Set. We assume we are considering a polyhedral structure composed of n atoms or vertices which are connected to each other by bonds or edges. Each vertex may carry an external ligand or lone pair of electrons. These may be viewed as part of the vertex, and we will not consider their contribution to polyhedral bonding. Each vertex provides three of its four valence orbitals to be involved in cluster bonding: an internal or radial orbital, denoted by p_z in Figure 1, and two tangential orbitals, shown as p_x and p_y. The fourth valence is an external radial orbital which forms a localized bond with an external ligand or carries a lone pair of electrons. Since the external orbitals do not directly affect cluster bonding, they are neglected in this 3-dimensional Hückel theory for clusters. Thus there is a basis set of $3n$ AOs $\{\chi_r\}$ from which a set of $3n$ MOs $\{\phi_i\}$ may be constructed as linear combinations of the AOs: $\phi_i = \sum c_{ri}\chi_r$. The terms radial and tangential are related to the choice of the local coordinate system for each vertex and will be described below.

B. Hückel Approximations. The development of Hückel theory involves three basic types of integrals: AO overlap, S; Coulomb, α; resonance, β:

(15) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563.
(16) Fowler, P. W.; Porterfield, W. W. *Inorg. Chem.* **1985**, *24*, 3511.

$$S_{ij} = \langle \chi_i | \chi_j \rangle$$

$$\alpha_i = \langle \chi_i | H | \chi_i \rangle$$

$$\beta_{ij} = \langle \chi_i | H | \chi_j \rangle$$

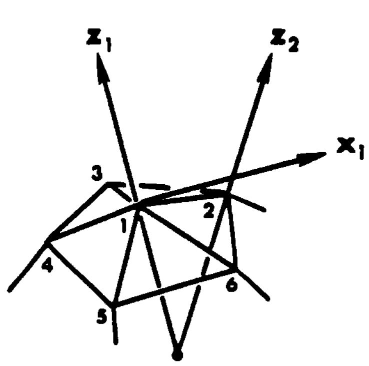
In this model, normal Hückel approximations hold. All AOs are normalized to unity but overlap integrals between different AOs are taken as zero:

$$S_{ij} = \begin{cases} 1, & i = j \\ 0 & i \neq j \end{cases}$$

In the Hückel treatment of planar conjugated molecules, the Coulomb integrals α_i are the same for all atomic orbitals, $\alpha_i = \alpha$, and consequently α is often taken as the zero of energy, or $\alpha = 0$. On this scale, all MOs with negative energies are bonding and those with positive energies are antibonding. In 3-dimensional Hückel theory we wish to distinguish between Coulomb integrals for radial and tangential orbitals. Therefore we designate α_R as the coulomb integral for radial orbitals and α_T as the coulomb integral for tangential orbitals. To readjust the zero of energy so we can interpret MOs as either bonding or antibonding by the sign of the orbital energy, we require $\alpha_R + 2\alpha_T = 0$, where α_T is doubly weighted to account for the fact that there are twice as many tangential orbitals as there are radial orbitals. We can express the difference between the two Coulomb integrals as a function of a standard resonance integral β: $\delta\alpha = \alpha_R - \alpha_T = k\beta$ where k is an adjustable parameter.

The resonance integral β_{ij} between bonded or adjacent vertices i and j is one of four standard types if the orientations of the AOs correspond to one of the four standard combinations shown in Figure 1: radial type (Figure 1a), denoted by β_1; tangential σ type (Figure 1b), β_2; tangential π type (Figure 1c), β_3; and radial–tangential σ type (Figure 1d), β_4. For convenience, we assume hereafter $\beta_1 = \beta_2 = \beta_3 = \beta_4 = \beta$. Resonance integrals for other orientations depend on the local coordinate system described below. As in 2-dimensional Hückel theory, $\beta_{ij} = 0$ for all cases for which AOs i and j are not on neighboring atoms.

C. Local Coordinate System. The local coordinate system on each vertex is set such that its z axis projects outwardly from the center of the polyhedron and its x axis points toward the z axis of one of its neighbors. Although this choice of local coordinate



system is not unique, the many different possible choices give the same result. Under this definition p_z AOs are equivalent to radial orbitals and p_x and p_y AOs are tangential orbitals. Meanwhile, assume that all neighboring vertices are equally spaced on the perimeter of a circle centered on our atom of choice. Suppose vertex i has l neighbors (labeled j_m, $m = 1, ..., l$) around it. Then we could rotate $2\pi(m-1)/l$ about the z axis of the central vertex i so that its x axis points to each vertex j_m sequentially starting from vertex j_1. Figure 2 shows such a transformation.

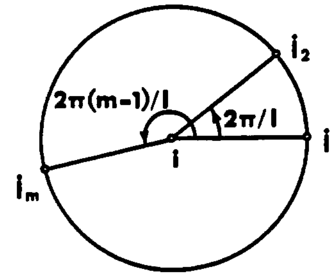


Figure 2. Polyhedral vertex i surrounded by n adjacent vertices $j_1, j_2, ..., j_n$ arranged around i at equal angles.

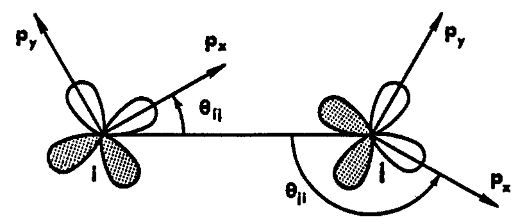


Figure 3. General orientations of p_x and p_y orbitals on vertices i and j.

The resonance integrals can be expressed as follows:

$$\beta_{ij}(p_x\text{–}p_x) = (\cos\theta_{ij})(\cos\theta_{ji})\beta_2 - (\sin\theta_{ij})(\sin\theta_{ji})\beta_3$$

$$\beta_{ij}(p_x\text{–}p_y) = (\cos\theta_{ij})(\sin\theta_{ji})\beta_2 + (\sin\theta_{ij})(\cos\theta_{ji})\beta_3$$

$$\beta_{ij}(p_y\text{–}p_x) = (\sin\theta_{ij})(\cos\theta_{ji})\beta_2 + (\cos\theta_{ij})(\sin\theta_{ji})\beta_3$$

$$\beta_{ij}(p_y\text{–}p_y) = (\sin\theta_{ij})(\sin\theta_{ji})\beta_2 - (\cos\theta_{ij})(\cos\theta_{ji})\beta_3$$

$$\beta_{ij}(p_z\text{–}p_z) = \beta_1$$

$$\beta_{ij}(p_z\text{–}p_x) = \beta_4$$

where θ_{ij} and θ_{ji} are the phase angles defined in Figure 3. For the regular polyhedra such as octahedron, cube, and icosahedron, the equiangular assumption is exact, but in other structures it is only approximate. The assumption may be rather poor for polyhedra that contain square or pentagonal faces. To make the choice of phase angles somewhat less arbitrary, we introduce a structural model that we call the deltahedral frame. For structures containing square or pentagonal faces, we cap each such face with a dummy atom to produce a deltahedron and we use this deltahedral frame for the purposes of calculating phase angles between tangential orbitals. The deltahedral frame will allow us to extend the 3-dimensional Hückel method to treat *nido*, *arachno*, and nonpolyhedral cluster shapes. The dummy atoms serve only to establish local coordinates, and no dummy atom atomic orbitals are involved in energy calculations.

These procedures have been programmed in FORTRAN to run on an IBM PS/2 Model 50 computer. The program will be made available to the scientific community through other channels.

Applications to the *closo*-Boranes

The *closo*-boranes, $B_nH_n^{2-}$, $n = 5$–12, constitute a series of ions with elegant polyhedral forms.[17] Although the $n = 5$ member of the series has never been prepared, the corresponding isoelectronic and presumably isostructural *closo*-carborane $C_2B_3H_5$ is known and it has the shape of a trigonal bipyramid. $B_5H_5^{2-}$ is expected to have the same shape. The known *closo*-borane structures are all *deltahedra*, polyhedra whose faces are all triangles. The preference for triangles can be rationalized from arguments based

(17) Williams, R. E. Carboranes. In *Progress in Boron Chemistry*, Vol. 2; Brotherton, R. J., Steinberg, H., Eds.; Pergamon: Oxford, U.K., 1970.

Table I. 3-Dimensional Hückel Total Energies (in Units of β) for $B_nH_n^{2-}$ in Various Polyhedral Forms

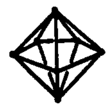
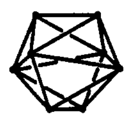
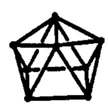
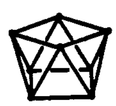
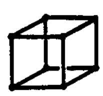
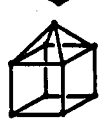
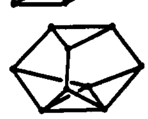
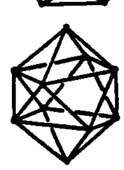
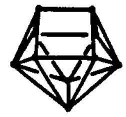
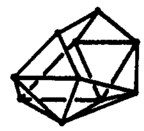
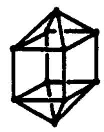
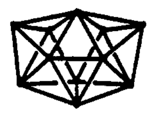
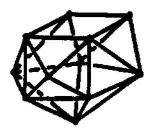
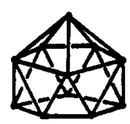
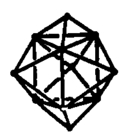
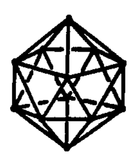
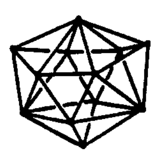
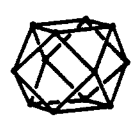
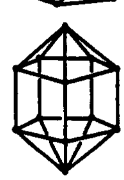
polyhedron size, *n*	polyhedral form		no. of bonds	no. of bonding orbitals	tot. energy
5	trigonal bipyramid		9	6	−17.0781
	square pyramid		8	7	−16.0000
6	octahedron		12	7	−22.0000
	trigonal prism		9	9	−17.5083
	pentagonal pyramid		10	8	−17.3552
7	pentagonal bipyramid		15	8	−26.3521
	capped octahedron		15	9	−25.1894
	capped trigonal prism		13	10	−21.2532
8	bidisphenoid		18	9	−30.4986
	bicapped trigonal prism		17	10	−29.2946
	square antiprism		16	10	−26.7701
	cube		12	12	−21.0000
9	tricapped trigonal prism		21	10	−34.7375
	capped square antiprism		20	11	−33.1548
	capped cube		16	12	−27.4512
	tridiminished icosahedron		15	13	−27.3801
10	bicapped square antiprism		24	11	−39.3190

Table I (Continued)

polyhedron size, *n*	polyhedral form		no. of bonds	no. of bonding orbitals	tot. energy
	sphenocorona		22	12	−36.5257
	bidiminished icosahedron		20	13	−34.2152
	bicapped cube		20	12	−33.8892
11	octadecahedron		27	12	−43.3669
	scarabheptadecahedron		26	12	−42.3209
	capped pentagonal antiprism		25	13	−41.0132
	pentacapped trigonal prism		27	15	−39.5941
12	regular icosahedron (I_h)		30	13	−48.2148
	icosahedron (D_{3h})		30	13	−47.2381
	cuboctahedron (O_h)		24	13	−41.4249
	bicapped pentagonal prism (D_{5h})		25	15	−40.7118

on bond energies and Euler's theorem. More bonds between atoms should increase the stability of the molecule. If a polyhedral cluster had a square face, then an additional bond or edge would close the square into two fused triangles, giving a more stable structure. All larger polygons can be subdivided into triangles by adding edges. But the triangle can be subdivided no further so the triangle represents the ultimate in edge-forming capability. Euler's theorem, $e = n + f - 2$, relates numbers of edges *e*, vertices *n*, and faces *f*. For a given *n*, more faces give more edges.

Perhaps the most significant test of the 3-dimensional Hückel method is whether for a given *n* it can correctly select the known structure from among a set of plausible polyhedral structures. Table I contains the total energies of various polyhedral forms for $B_nH_n^{2-}$ calculated by the 3-dimensional Hückel method. The $B_nH_n^{2-}$ polyhedra contain $n + 1$ skeletal electron pairs. For each *n*, we have calculated two or more polyhedral structures. In each case we have chosen, besides the known structure, one or more additional structures proposed by Fuller and Kepert, who predicted relative energies of polyhedral structures using an empirical potential model.[18] In each case, n = 5–12, the 3-dimensional Hückel method correctly gives the lowest total energy to the experimentally known or expected shape. Furthermore, the lowest energy structure for each *n* has $n + 1$ bonding MOs that are completely occupied by electrons while all antibonding MOs are

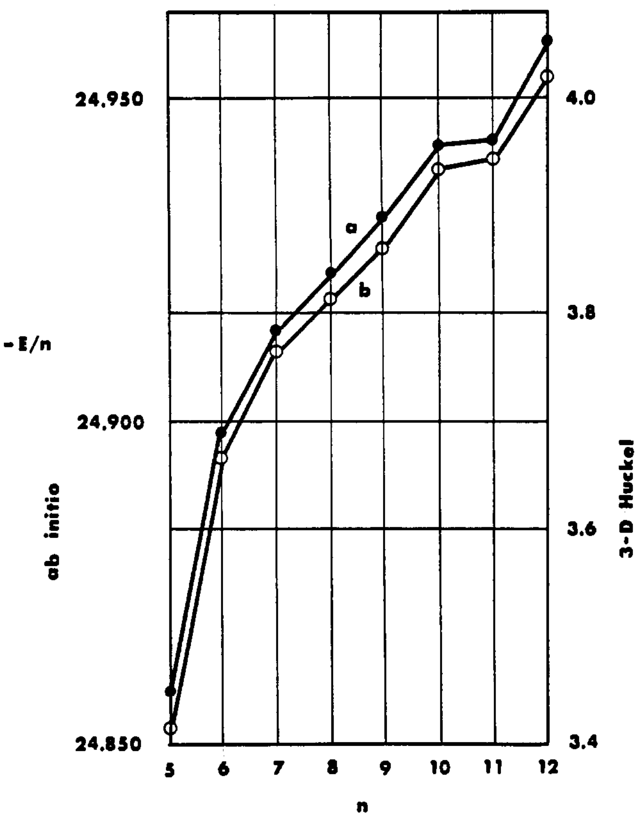


Figure 4. Ratio of total energy E to polyhedral size n as a function of n for $B_nH_n^{2-}$ from (a) *ab initio* calculations and (b) 3-dimensional Hückel theory.

vacant, confirming the $n + 1$ cluster electron pair rule. For each n, the lowest energy structure is also the one with the largest number of polyhedral bonds or edges, following the rule that the most stable structure should have the largest number of edges or faces, although there are a few exceptions. For $n = 7$, 11, and 12, two structures have the same maximum number of bonds and the 3-dimensional Hückel method correctly gives the lower energy to the known structure. Generally, structures with the same numbers of bonds have similar energies. There are a few cases in which a structure with fewer bonds has a lower energy than one with more bonds. For $n = 6$, the trigonal prism with 9 bonds, has lower energy than the pentagonal pyramid, with 10 bonds. For $n = 11$, the pentacapped trigonal prism, 27 bonds, has higher energy than structures containing 25 and 26 bonds. For $n = 12$, the cuboctahedron, 24 bonds, has lower energy than the bicapped pentagonal prism, 25 bonds.

We can compare reuslts of 3-dimensional Hückel theory with those of geometry-optimized *ab initio* SCF MO calculations at the STO-3G level.[19] Our first comparison is of the quantity $-E/n$, the total energy of the ion divided by the number of vertices n. Figure 4 shows that the 3-dimensional Hückel results closely parallel the *ab initio* results. Obviously, quantitative comparisons between the two methods are impossible. In constructing Figure 4, we chose scales for the two sets of data that make end points of the two curves fall in about the same place. Remarkably similar trends through the two series follow the oft-noted empirically observed trend of increasing stability of $B_nH_n^{2-}$ with polyhedron size n.[20]

Total energies from geometry-optimized AM1 and *ab initio* SCF-MO (STO-3G) calculations are available for four different isomeric structures of $B_{12}H_{12}^{2-}$: regular icosahedron (I_h), icosahedron (D_{3h}), cuboctahedron (O_h), and bicapped pentagonal prism

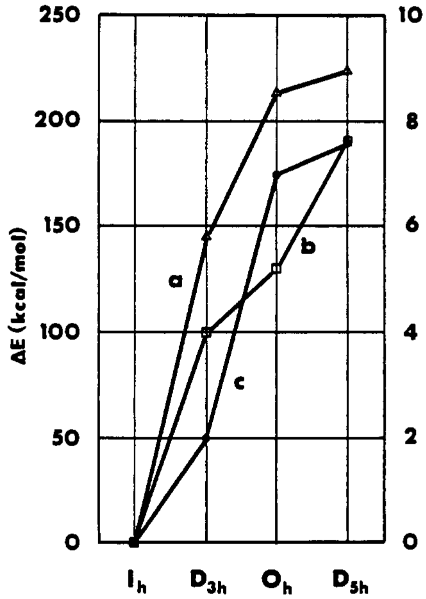


Figure 5. Relative energies of $B_{12}H_{12}^{2-}$ isomers as obtained by (a) *ab initio* calculations, (b) AM1 semiempirical SCF, and (c) 3-dimensional Hückel theory. The three methods give the same order of relative stabilities of the four isomers: $I_h > D_{3h} > O_h > D_{5h}$.

(D_{5h}).[21] Figure 5 compares relative energies of these structures as determined by *ab initio*, AM1, and 3-dimensional Hückel methods. Results from the three methods agree qualitatively through this series, with the regular icosahedron being the most stable and the bicapped pentagonal prism the least stable.

Still another comparison of *ab initio* and 3-dimensional Hückel methods is among calculated charge densities on the borons of $B_nH_n^{2-}$ polyhedra, and these are given in Figure 6. The *ab initio* results are all-electron Mulliken net atom populations;[19] the 3-dimensional Hückel results are Coulson charge densities. Since the *ab initio* calculations include hydrogen substituents and the larger part of the extra electron charge is distributed over the more electronegative hydrogens, the absolute values of the calculated charges on the borons are considerably smaller than those from the Hückel calculations, in which hydrogen substituents are ignored. For the regular octahedron and regular icosahedron, $n = 6$ and 12, respectively, all atoms are equivalent, and therefore all charges are equal. Each of the other polyhedra has at least two different sets of equivalent atoms, and in the cases of $n = 5$, 7, 8, 9, and 10, the two models agree on the relative order or size of negative charge. The $n = 11$ example is more complicated because the low symmetry of this polyhedron exhibits five different kinds of sites, each of which may be expected to have a different charge. *Ab initio* and 3-dimensional Hückel results agree that the two four-coordinate sites (2 and 3) should carry the largest negative charges. One can argue from traditional valence theory that these sites, which have fewest neighbors with which electrons must be shared, should have the largest electron densities. Similarly, the unique six-coordinate site (1), which has the largest number of neighbors, would be expected to have the smallest electron density which is, indeed, the result of the *ab initio* calculations. The 3-dimensional Hückel results give site 1 only the second smallest charge. If one has reservations concerning the reliability of 3-dimensional Hückel results, keep in mind the problems associated with limited basis set *ab initio* calculations which other experience shows may be very sensitive to the choice of the basis set. The $n = 11$ case is a particularly tough test for both methods. The rule of topological charge stabilization makes use of relative charges on the vertices of homoatomic clusters to

(18) Fuller, D. J.; Kepert, D. L. *Inorg. Chem.* **1982**, *21*, 163; *Polyhedron* **1983**, *2*, 749.
(19) Ott, J. J.; Gimarc, B. M. *J. Comput. Chem.* **1986**, *7*, 673.
(20) Housecroft, C. E.; Wade, K. *Inorg. Chem.* **1983**, *21*, 1391.
(21) Gimarc, B. M.; Warren, D. S.; Ott, J. J.; Brown, C. *Inorg. Chem.* **1991**, *30*, 1598.

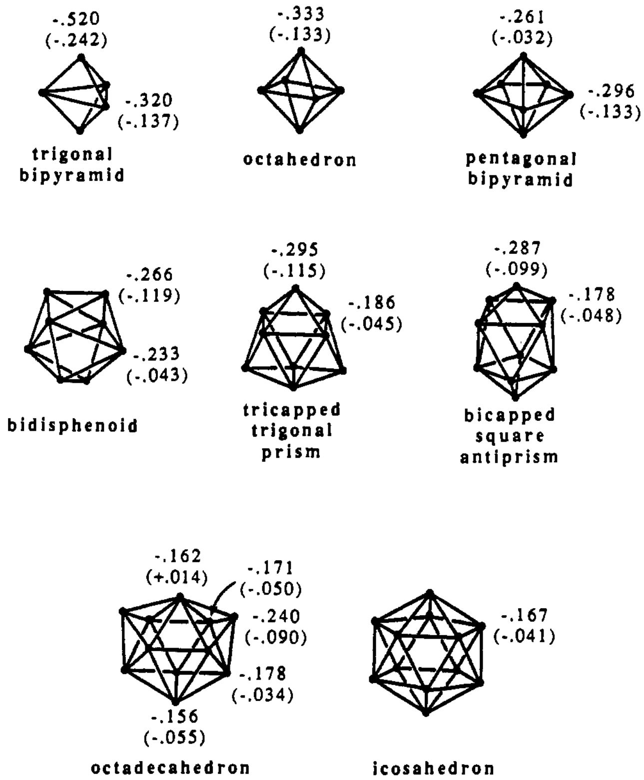


Figure 6. Comparisons of calculated charge densities at borons in *closo*-boranes, $B_nH_n^{2-}$, as obtained from 3-dimensional Hükel theory and from *ab initio* calculations at the STO-3G level (values in parentheses). The *ab initio* values are smaller because much of the charge is distributed over the *exo*-hydrogens which are neglected in the 3-dimensional Hückel model.

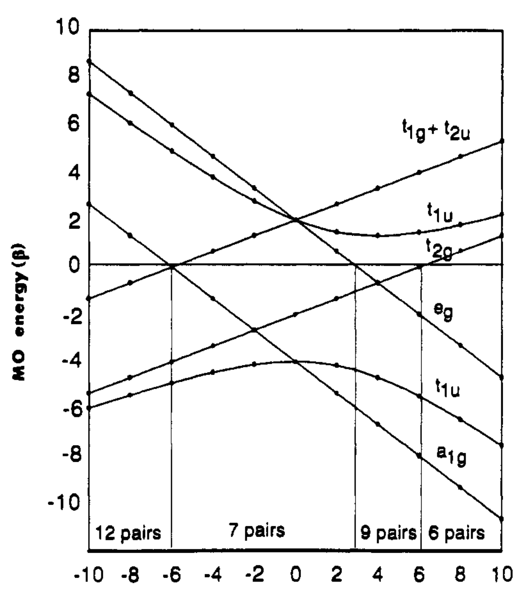


Figure 7. Octahedral cluster MO energy levels as functions of $\delta\alpha = k\beta$, the difference in Coulomb integrals for radial and tangential AOs. Bonding orbitals have negative energies; antibonding orbitals are positive.

predict relative stabilities of positional isomers of isoelectronic, isostructural heteroatomic analogs.[22]

Applications to Transition Metal Clusters

The polyhedral skeletal electron pair approach presented by Mingos and Wade provides a simple way to understand the structural diversity of various polynuclear molecules of both main

(22) Ott, J. J.; Gimarc, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4303.

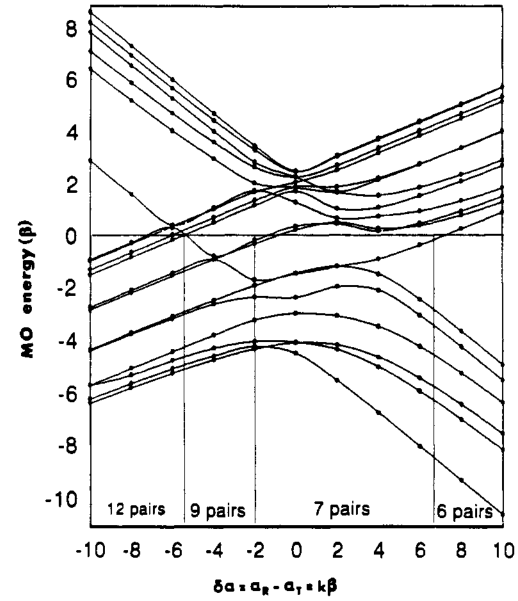


Figure 8. Capped square pyramidal MO energy levels as functions of the difference in Coulomb integrals $\delta\alpha$ between radial and tangential AOs.

group and transition metal atoms. Teo and co-workers developed an alternative qualitative method to deal with the same theme.[23] Accurate MO calculations have been reported for many individual clusters. In this section we use 3-dimensional Hückel theory to explain the structural characters shown by transition metal clusters.

We assume that the transition metal atom in a cluster, like the main group atom, has three AOs that are involved in cluster bonding. This assumption is ensured by the famous isolobal principle.[24,25] The three AOs consist of one radial orbital and a degenerate pair of tangential orbitals. The relative energies or Coulomb integrals α_R and α_T for radial and tangential orbitals, respectively, may be different from metal to metal and perhaps from ligand to ligand. Therefore we admit the parameter $\delta\alpha = \alpha_R - \alpha_T = k\beta$, such that $\alpha_R + 2\alpha_T = 0$. In addition, d-type orbitals in transition metals are involved in weaker bonding than s- or p-type orbitals of main group atoms, so for transition metal clusters, we assume that direct interactions among d orbitals can be neglected and that any of their effects can be included through changes in Coulomb integrals (α) of s and p orbitals. For a particular polyhedron, the first-order correction to the MO energy levels is largely proportional to the change of Coulomb integrals. Therefore it is reasonable to focus only on the difference of Coulomb integrals and its effect on the electronic structure and thereby the properties of transition metal clusters. As a test of 3-dimensional Hückel theory, we consider here 6-atom clusters in octahedral, capped square pyramid, trigonal prism, and pentagonal pyramid structures.

A. Octahedral Clusters. Octahedral structures are common among transition metal clusters. Some examples have numbers of pairs of cluster bonding electrons that differ from $n + 1 = 7$:

no. of cluster electron pairs	known octahedral clusters
6	$[Mo_6Cl_{14}]^{2-}$
7	$Rh_6(CO)_{16}$, $[Fe_6C(CO)_{16}]^{2-}$
9	$Ni_6(\eta^5\text{-}C_5H_5)_6$, $[Fe_6S_8(PEt_3)_6]^{2+}$

3-Dimensional Hückel theory can be used to explain why clusters with these numbers of electron pairs are stable. For a stable

(23) Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251. Teo, B. K.; Longoni, G.; Chung, F. R. K. *Inorg. Chem.* **1984**, *23*, 1257.
(24) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.
(25) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

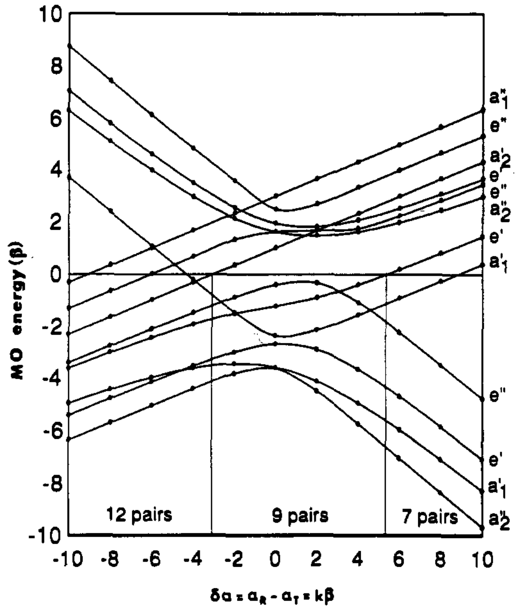


Figure 9. Trigonal prism MO energy levels as functions of $\delta\alpha$.

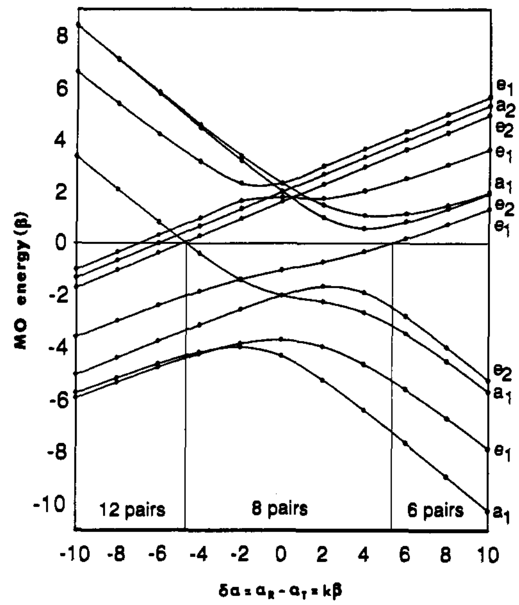


Figure 10. Pentagonal pyramid MO energy levels as functions of $\delta\alpha$.

structure, the cluster bonding electrons completely fill the bonding MOs while nonbonding and antibonding MOs are empty. As a variable parameter we use the difference between Coulomb integrals for radial and tangential orbitals: $\delta\alpha = \alpha_R - \alpha_T = k\beta$. Figure 7 plots calculated energy levels of MOs of the octahedron as functions of $k\beta$. Bonding MOs have negative energies; antibonding orbital energies are positive. The diagram shows that, for $-6\beta \leq \delta\alpha \leq +3\beta$, 7 electron pairs completely fill the bonding MOs. For $+3\beta \leq \delta\alpha \leq +6\beta$, it takes 9 pairs to fill the bonding levels. For $\delta\alpha \geq +6\beta$, 6 pairs fill the bonding levels.

B. Capped Square Pyramidal Clusters. The complex $Os_6H_2(CO)_{18}$ is an example of a triangular face capped square pyramidal cluster with 7 cluster electron pairs. Figure 8 displays MO energies as functions of $\delta\alpha$ for the capped square pyramid. For $-2\beta \leq \delta\alpha \leq 6\beta$, 7 electron pairs occupy the bonding orbitals and all antibonding orbitals are vacant. For $-6\beta \leq \delta\alpha \leq -2\beta$, it takes 9 electron pairs to fill completely the bonding MOs.

C. Trigonal Prism Clusters. Examples of trigonal prism clusters are as follows:

no. of cluster electron pairs	known trigonal prism clusters
7	$[Pt_6(CO)_{12}]^{2-}$
9	$[Rh_6C(CO)_{15}]^{2-}$; $[Co_6N(CO)_{15}]^-$

Figure 9 shows how trigonal prism MO energies vary with $\delta\alpha$. For $+5\beta \leq \delta\alpha \leq +8\beta$, 7 electron pairs completely fill the bonding MOs. For $-3\beta \leq \delta\alpha \leq +5\beta$, the bonding orbitals are filled by 9 electron pairs.

D. Pentagonal Pyramid Clusters. No clusters of pentagonal pyramidal shape are known. Figure 10 shows how MO energies change with $\delta\alpha$. In the interval $-5\beta \leq \delta\alpha \leq +5\beta$, it takes 8 pairs to fill completely all bonding MOs. Previous examples suggest that this range of $\delta\alpha$ is the most important one for transition metal clusters. Therefore we predict that if a pentagonal pyramid cluster is ever prepared, it will most likely contain 8 cluster electron pairs.

Conclusions

In the applications we have described, the 3-dimensional Hückel method has successfully selected the correct deltahedral structures from among a set of plausible polyhedra for the *closo*-boranes, $B_nH_n^{2-}$. Each of the favored structures was found to have $n + 1$ bonding orbitals, confirming the observed rule that these structures contain $n + 1$ skeletal electron pairs. The simple Hückel method projects a trend of increasing stability with larger polyhedral size n, in agreement with experimental and *ab initio* results. Among a group of four isomeric structures for $n = 12$ for which *ab initio* energies have been reported, the three-dimensional Hückel theory produces the same order of stabilities. Trends in calculated charge densities agree rather well with those based on *ab initio* wave functions. Finally, for a set of six-atom transition metal polyhedra, the introduction of an adjustable parameter $\delta\alpha$, the difference between Coulomb integrals for radial and tangential orbitals, provides a means for rationalizing different numbers of skeletal bonding electron pairs that have been proposed for clusters that are known to have these structures.

The virtue of Hückel theory lies in its stark simplicity. Its success does not depend on astute choices of calibration parameters, basis sets, or the extent of electron correlation corrections. The successful descriptions of cluster property trends by 3-dimensional Hückel theory are results of molecular connectivity and electron count, two very simple and chemically appealing concepts.

Acknowledgment. We are grateful to the National Science Foundation for partial support of this research through Grant No. CHE-9012216 to the University of South Carolina.