Electronic Structure of Clusters

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Glossary

Ab initio calculations: attempt to calculate from first principles, without use of empirical data, solutions to Schrödinger's equation

Deltahedron: a polyhedron with only triangular faces

Abbreviations

DFT = Density Functional Theory; DSD = Diamond-Square-Diamond; HOMO = Highest Occupied Molecular Orbital; IR = Irreducible Representation; LCAO = Linear Combination of Atomic Orbitals; Ph = Phenyl; PSEPT = Polyhedral Skeletal Electron Pair Theory; SCF = Self-Consistent-Field; SDDS = Square-Diamond, Diamond-Square; TSH = Tensor Surface Harmonic.

1 INTRODUCTION

The first problem encountered in writing an article of this kind lies in deciding what a *Cluster* actually is, and which sorts of cluster are relevant to the audience in question. The former problem may be addressed in terms of size or number of constituent atoms; for example, Sugano¹ considers a classification in terms of molecules, microclusters, and fine particles. On the other hand, Berry has distinguished clusters as 'finite aggregates whose composition can be changed by adding or taking away units of the species that comprise them... they are finite bits of what, in composition but not necessarily in structure, constitute a tiny sample of bulk

material, but more than a single molecule or even two atoms or molecules'.² Here, we must recognize that the domain of cluster chemistry extends beyond systems such as boranes, carboranes, and transition metal carbonyls, which are generally considered to be the stuff of inorganic cluster chemistry.^{1,3–5} These are certainly the molecules of primary interest here, but it would be shortsighted to ignore the connections between these species and clusters bound, for example, by van der Waals forces. There is often much to be learned from making such comparisons: for instance, we may find analogous structures and rearrangement mechanisms in clusters bound by quite different forces. The converse is also true, and a better understanding of the dynamics of small inert gas clusters has been achieved partly by the application of ideas that originated in inorganic chemistry concerning rearrangement mechanisms.⁶

To appreciate the ubiquity of clusters in chemistry and physics, one need only consult the proceedings of one of the biennial International Symposia on Small Particles and Inorganic Clusters (ISSPIC).⁷ These volumes include species ranging from hydrocarbon polyhedra, such as dodecahedrane⁸ (*see also Dodecahedral*), to large carbon clusters,⁹ and from small inert gas clusters to colloidal metal particles containing thousands of atoms. These systems are of interest for a variety of reasons, such as the investigation of fundamental processes including melting and freezing, and can sometimes provide insight into the behavior of larger systems at a more tractable level. Furthermore, small clusters may exhibit properties that are unique to the intermediate size regime, which may be of technological importance.¹⁰

The principal subject of this contribution is the electronic structure of clusters, and so we shall mainly be concerned with molecules in which the interatomic forces cannot be well described by simple empirical potential energy functions. Hence, the following section provides an overview of the progress that has been made in performing quantum mechanical calculations for clusters. Major difficulties remain to be solved in this field, particularly with regard to systems containing Transition Metals. However, although accurate calculations are certainly important, there are various patterns concerning the correlation between structure and electron count, which require a more general explanation. The latter are considered in Section 3, and the various models that have been developed to explain them are reviewed in Section 4. One of these, Stone's Tensor Surface Harmonic (TSH) theory, is then developed in Section 5, and some further applications to cluster rearrangements are described in Section 6.

2 COMPUTATIONAL APPROACHES

It is certainly not the purpose of this section to describe the mechanics of ab initio quantum chemical calculations on clusters.¹¹ However, some understanding of the problems and achievements in this field is necessary to appreciate the simpler general models described in subsequent sections. Even if extensive and accurate calculations were possible for all the inorganic clusters of interest, the latter models would still be needed to explain the structural patterns that have been deciphered.

Most applications of ab initio quantum chemistry involve expanding the wavefunction using a basis set of atomic orbitals. As the many-body problem is not analytically tractable in either classical or quantum mechanics, we can never obtain the exact wavefunction. However, the variation principle¹² tells us that the more basis functions we use, the more accurate our calculation should become. Unfortunately, the computational cost of the most commonly employed selfconsistent-field¹² (SCF) method increases roughly as N^4 , where N is the number of basis orbitals. Hence, for clusters containing Transition Metals, for which even a minimal basis set of atomic orbitals requires many functions, the calculations rapidly become impossible. There is another problem as well: the usual Hartree-Fock SCF procedure neglects the instantaneous electron-electron interaction, replacing it instead with an average field^{12,13} (see Hartree-Fock Theory). The error incurred by this treatment of the electron correlation problem generally becomes more significant for systems with low-lying electronic states, as are commonly found in transition metal compounds. Density functional theory¹⁴ (DFT) can help deal with the correlation problem, but the reliability of such calculations is often subject to debate. This is particularly true for molecules containing heavy elements, where relativistic effects are also important.¹⁵

Given this background, it is not surprising that many different approaches, all introducing further approximations,¹⁶ have been applied to inorganic clusters. The two most commonly encountered approaches in this area are the Extended Hückel¹⁷ and Fenske–Hall¹⁸ methods (*see also Extended Hückel Molecular Orbital Theory*). The former is the simplest approach, making use of empirical data, while the latter uses no experimental information, but instead approximates the quantum mechanical Hamiltonian so as to avoid many of the most time-consuming integrals. Despite the sweeping assumptions used in these methods,¹⁹ they have often been found to give valuable insights, although DFT is now commonly used instead.

The early DFT studies of main group clusters by Jones and coworkers should be mentioned here.²⁰ However, as these are primarily concerned with clusters that are describable in terms of two-center, two-electron bonds, they will not be considered further. For similar reasons, no attempt will be made to survey the rapidly growing body of calculations on carbon–fullerene systems⁹ (see Carbon: Fullerenes). The σ -bonding framework of these molecules is again easily understood from the point of view of electron counting. Predicting for which geometries the delocalized π -system is especially favorable is a more interesting problem, but is beyond the scope of this review. Some other specific calculations on boranes, carboranes, metal, and silicon clusters will be considered in the following sections.

3 EMPIRICAL STRUCTURE-ELECTRON COUNT CORRELATIONS

With the explosion in size of the database of known cluster compounds, it is reassuring to note that a number of patterns were soon recognized and exploited by inorganic chemists. The most important relationships between geometry and the number of electrons in a cluster ('electron-counting rules', see *Counting Electrons*) are summarized in the Debor Principle²¹ (or *Wade's Rules*), Polyhedral Skeletal Electron Pair Theory²² (PSEPT), and the Isolobal Principle.²³ These 'rules' (to which there are various exceptions) include three-connected clusters (By convention, the connectivity' of a vertex is the number of nearest-neighbors in the cluster cage, not counting terminally bound ligands.), like prismane, deltahedral clusters (which have only triangular faces), such as closo-boranes; 'naked' clusters²⁴ like Sn_5^{2-} and Pb_5^{2-} ; clusters with interstitial atoms, fused molecules, which can be decomposed into deltahedra that share vertices, edges, or faces, and even large multispherical transition metal clusters. Much of the rest of this article is devoted to rationalizing these patterns, whose importance can perhaps be appreciated by the example of Au₁₃Cl₂(PMe₂Ph)₁₀³⁺. This compound was successfully synthesized several years after the stability of gold clusters $Au_{13}(PR_3)_{12}^{5+}$ was predicted on the basis of simple bonding considerations.25

Some of the historical development of the electroncounting rules is summarized in a review by Mingos and Johnston;²⁶ here, we will concentrate on the patterns themselves, beginning with the simplest cases – more details can be found elsewhere.²⁷ The most straightforward clusters commonly encountered in inorganic chemistry are those that can be described by essentially localized two-center, twoelectron bonds, where all the atoms obey an effective atomic number rule EAN Rule. For main group atoms, this means that each one is associated with 8 valence electrons to give an 'inert gas configuration'; for *Transition Metals*, 18 electrons are usually required to do this. Hence, such clusters are associated with

$$N_e = 8n - 2E$$
 main group or
 $N_e = 18n - 2E$ transition metal (1)

where N_e is the number of valence electrons, *n* is the number of vertices in the cluster, and *E* is the number of twocenter, two-electron bonds, or edges. For ring compounds, E = n and hence $N_e = 6n/16n$ for main group/transition metal clusters. Three-connected *Polyhedral* systems, such as prismane, have E = 3n/2 so that $N_e = 5n/15n$. To cover mixed compounds, we note that replacement of a main group vertex atom by a transition metal should increase N_e by 10, while interstitial atoms are generally not associated with an increase in the number of occupied molecular orbitals,²⁷ and effectively act as electron donors. The relatively simple consequences of interchanging main group and transition metal atoms basically follow from the symmetries of the orbitals that these fragments provide for skeletal cluster bonding, as identified in the Isolobal Principle of Hoffmann and collaborators.²³

Most clusters, however, cannot be described adequately in terms of two-center, two-electron bonds because the connectivity of the vertices exceeds the number of valence orbitals that are available for bonding. Early efforts to rationalize such systems, such as Lipscomb's styx approach²⁸ and Kettle's Topological Equivalent Orbital Method,²⁹ are described by Mingos and Johnston.²⁶ In these more difficult cases, the simple valence-bond picture is inappropriate; examples are deltahedral clusters composed of B–H vertices or conical M(CO)₃ fragments, both of which usually have only three orbitals available for skeletal bonding. Theoretical models for describing these systems will be discussed in the next section.

We find that four-connected clusters and *closo*-deltahedra have $N_e = 4n + 2/14n + 2$ for main group/transition metal clusters. *Closo*-deltahedra are clusters with entirely triangular faces; however, some four-connected clusters have one or more square faces.²⁷ When successive vertices are (notionally) removed from a *closo*-deltahedron, the resulting molecules are called nido, arachno, hypho, and so on. The Debor Principle²¹ (or *Wade's Rules*) recognizes that the total number of valence electrons in such systems does not change, and in terms of the number of vertices remaining, *n*, this gives $N_e = 4n + 4/14n + 4$, 4n + 6/14n + 6,... for main group/transition metal nido, arachno, ... clusters.

Most of the remaining patterns might be classified under the heading of 'condensation rules,' many of which were developed by Mingos and coworkers. The Capping Principle states that the number of skeletal bonding orbitals is unchanged when one face of a *Polyhedral* cluster is capped.^{22,30} Hence, if the capping moiety is a conical M(CO)₃ fragment, then N_e increases by 12, this being the number of electrons in the nonbonding and metal-ligand bonding orbitals.²⁶ The Principle of Polyhedral Fusion deals with clusters that can be (notionally) decomposed into two polyhedra (A and B) that share a vertex, edge, or face.³¹ In this case, N_e is usually equal to the sum of $N_e(A)$ and $N_e(B)$, regarded as complete, individual entities each containing copies of the fragments that are shared between them, minus the number of valence electrons expected for the shared unit.26 The final one of these 'principles' is that of polyhedral inclusion, where high nuclearity multispherical systems are considered in terms of encapsulated polyhedra.³² However, as a number of subcases

must be considered for such systems, the reader is referred elsewhere for details. 27,32

The remainder of this article is largely concerned with describing how some of the above observations can be rationalized using Stone's Tensor Surface Harmonic theory, and with the further implications of this model for dynamical processes such as cluster rearrangements. The number of example systems and electron count rationalizations will be kept relatively small in favor of explaining the theoretical foundations that underlie the method. Tables of examples and more detailed analyses of the various cases may be found elsewhere.^{26, 27}

4 MODELS OF CLUSTER BONDING

To achieve a general understanding of the patterns described in the previous section requires some sort of model for the energy of a cluster as a function of its geometry and the number of valence electrons. In this section, we focus upon the three most successful approaches, namely, jellium models, topological methods based upon graph theory, and Stone's Tensor Surface Harmonic (TSH) theory. In each case, the energetic problem is simplified by asking how many bonding, nonbonding, and antibonding orbitals are available for a given cluster geometry, and these orbitals may be delocalized, localized, or a mixture of both. In fact, TSH theory is more powerful than this, as it really defines an orbital transformation, which may be applied to the results of any calculation, as discussed below.

In each of the three approaches, we effectively guess the forms and energies of the solutions to the quantum mechanical many-body problem. Jellium models achieve this by solving a Schrödinger equation in which all the electron–electron and electron–nucleus interactions are replaced by a simple effective potential. The result is a set of spatially delocalized functions of increasing energy into which electrons are assigned by the usual Aufbau principle.¹² Although jellium methods are commonly found in the physics literature, they are of rather limited application in the present context, and are more appropriate for clusters of alkali or alkali earth metals, for which very large systems have been considered.

The topological or graph-theoretical approaches attempt to define the bonding and antibonding orbitals available to a cluster in terms of a sort of valence-bond description,¹² where hybridized atomic orbitals are directed in space to form either localized or multicenter functions. (*See also Hybridization.*) The analysis of a complex structure involving delocalized bonding may, however, require some seemingly subjective decisions about how the atomic orbitals overlap, where the multicenter bonds should be formed, and so forth. How is it then, that organic chemists, armed only with pencil, paper, and some knowledge of basic molecular orbital theory and the Woodward–Hoffmann rules,³³ can often successfully predict the outcome of apparently complex organic reactions? The simple answer is that the bonding in such systems is generally rather easier to describe than in clusters, and relatively accurate calculations may often be used for guidance. However, with the advent of TSH theory, the inorganic chemist now has tools that are similar in many respects to those used in organic chemistry. The increased difficulty of the analysis in inorganic clusters may then be seen as a consequence of delocalization occurring in three dimensions, and of the presence of d valence atomic orbitals in *Transition Metals*.

TSH theory may be regarded as either a descent-insymmetry approach, or, equivalently, as a method that exploits the existence of approximate quantum numbers in roughly spherical clusters. The idealized high-symmetry case in question is the free electron-on-a-sphere, for which the wavefunctions are the spherical harmonics, $Y_{LM}(\theta, \phi)$, and the angular momentum operators \hat{L}^2 and \hat{L}_z have corresponding good quantum numbers L and M_L . In a finite cluster, the Hamiltonian has lower symmetry appropriate to the point group in question. TSH theory assumes that approximately good quantum numbers still exist for the angular momentum of an electron about the center of a roughly spherical cluster, and exploits this assumption to approximate the molecular orbitals. The resulting linear combinations of atomic orbitals (LCAOs) would be the true molecular orbitals of the cluster if it actually had spherical symmetry; they are known as cluster orbitals. (See also LCAO Approximation.) However, the usefulness of TSH theory goes beyond this construction, in providing a transformation of basis that may be applied to the results of any calculation in which identifiable atomic orbitals are used. Despite the fact that the ideal linear combinations of TSH theory actually mix in real clusters, it is often true that they are still recognizable. This is the essence of an approximate quantum number.

Before developing the TSH approach in Section 5 to explain some of the structure-electron count correlations described above, we will first consider the connections between the jellium, topological, and TSH methods in a little more detail. It is noteworthy that none of these models in their usual form includes any attempt to allow for electron correlation. Hence, it is important to ask, for example, why TSH theory can explain all the general structure-electron count correlations so successfully. The answer is presumably that the correlation energy is often not of primary importance in discriminating between different geometries with the same number of electrons. However, sometimes there exists more than one low-energy structure associated with a given electron count; in such cases, and in any case where the correlation energy exhibits a large variation with geometry, we should anticipate exceptions to the usual 'rules'.

4.1 The Jellium Model

The jellium model was first developed by Knight *et al.*³⁴ to explain the 'magic numbers' observed in mass spectra of sodium and potassium clusters produced by supersonic expansion in molecular beams.³⁵ The method was adapted from nuclear physics, where 'magic number' nuclear states have been successfully explained.³⁶ If the potential energy vanishes inside a sphere and is infinite outside it, then the energetic ordering of the solutions to the resulting Schrödinger equation is

$$1s < 2p < 3d < 2s < 3f < 3p < 4g < 4d < 3s < 5h...,$$
(2)

where 3d, for example, has no radial nodes and two angular nodes and is fivefold degenerate. The notation is analogous to that used for atomic orbitals, though different from that used in some of the literature,³⁴ and seems appropriate in this context. The wavefunctions for any potential energy function that depends only upon the distance from a fixed origin may be written as a product of spherical harmonics¹² and functions that depend only upon the distance. Hence, the same degeneracies arise, because of the assumed spherical symmetry, as for an atom. It is noteworthy that differences in the order of these energy levels with a deep potential well only occur for relatively high-lying solutions.³⁷ Experimentally, peaks in the mass spectra of sodium and potassium clusters are indeed found for 8, 18, 20, 40, ... atoms, corresponding to completed electronic shells in the above scheme.³⁸

Various refinements of the above model have been proposed; for example, using alternative spherical potentials or allowing for nonspherical perturbations,39-40 and these can improve the agreement of the model with the abundance peaks observed in different experimental spectra. For small alkali metal clusters, the results are essentially equivalent to those obtained by TSH theory, for the simple reason that both approaches start from an assumption of zeroth-order spherical symmetry. This connection has been emphasized in two reviews,^{40,41} and also holds to some extent when considerations of symmetry breaking are applied. This aspect is discussed further below. The same shell structure is also observed in simple Hückel calculations for alkali metals, again basically due to the symmetry of the systems considered.⁴² However, the developments of TSH theory, below, and the assumptions made in the jellium model itself, should make it clear that the latter approach is only likely to be successful for alkali and perhaps alkali earth metals. For example, recent results for aluminium clusters have led to the suggestion that symmetry-breaking effects are more important in these systems.43

These conclusions are not unexpected. Firstly, the freeelectron approximation works best for the alkali metals, with significant deviations for divalent and trivalent metals.⁴⁴ Secondly, the LCAO-MO TSH treatment requires a more complicated treatment of p and d orbitals, involving tensor spherical harmonics. The jellium model makes no allowance for these properties, and hence, the analogy to TSH theory breaks down here. An alternative way to think about this breakdown is in terms of the strength of the nonspherical potential due to the nuclei,^{40,41} and its influence upon electrons that occupy effective single-particle states. As the orbital energy increases, so too does the de Broglie wavelength;¹² and the effect of the nonuniform distribution of nuclei becomes more significant. Splittings of the spherical symmetry degeneracies should therefore increase with the orbital energy, and will probably be greater for aluminium than, say, sodium, because for a given cluster geometry there are more valence electrons to accommodate. The former effect is apparent around the Highest Occupied Molecular Orbital HOMO and above in Hückel calculations on different cluster morphologies containing up to 1000 atoms.⁴⁵ One further viewpoint is obtained by considering the magnitude of matrix elements of the nuclear potential, expanded in terms of spherical harmonic components.41

Before leaving the jellium model, it seems appropriate to mention some results for sodium clusters of up to 22 000 atoms. The abundances observed can be explained in terms of the extra stability associated with both completed jellium shells (for less than about 3000 atoms) and with completed icosahedral or cuboctahedral geometric shells for larger sizes.⁴⁶ The results are especially interesting because of the observation of 'supershells' that occur because of an interference effect, which has been explained using semiclassical arguments.⁴⁷

One further question that one might naturally ask of metal clusters is how large they need to be for bulk properties to manifest themselves.⁴⁸ However, as the answer to this question depends crucially upon the bulk property in question, and the answer is still somewhat subjective, such issues will not be pursued here.

4.2 Topological Approaches

In the most well-developed topological approach, the mechanics of algebraic graph theory⁴⁹ are applied to enumerate the bonding and antibonding orbitals of a given cluster. From the earliest work of King and Rouvray,⁵⁰ the method has been extended by King,⁵¹ leading to a self-consistent framework for rationalizing the electron counts of many of the systems mentioned in Section 3, among others. Connections to TSH theory have been discussed in several studies.^{27,52} Basically, the method analyzes structures in terms of edge-localized, face-localized, and core-delocalized bonds that arise in the middle of cluster polyhedra. Electron pairs are then assigned to the resulting bonding orbitals, rather like the construction of a valence-bond wavefunction¹² when multicenter orbitals are included as building blocks.

This approach is perhaps best illustrated by a simple example. Consider a deltahedral cluster where the vertex connectivity is greater than three, for example, $B_6H_6^{2-}$. One

valence orbital per vertex is used to form a two-center, twoelectron bond to a terminal ligand (hydrogen in this case), leaving three orbitals, which may be partitioned into two functions that are tangential to the sphere on which the vertex atoms lie, and one which points toward the center of the cluster. Rationalization of the cluster electron count ($N_e = 4n + 2$) proceeds as follows. We already have *n* bonding orbitals corresponding to B–H bonds in this example. Pairwise overlap of the 2*n* tangential orbitals then produces *n* bonding and *n* antibonding sets, while overlap of the inward-pointing hybrids gives rise to one particularly low-lying orbital,⁵¹ giving a total of 2n + 1 bonding orbitals, which are completely filled by 4n + 2 electrons.

To describe edge-localized bonding, as in prismane, for example, the three valence orbitals left after terminal bonding are simply directed toward the three-neighboring vertices. This is not unreasonable, but for more complex systems, it may require some imagination to direct the various valence orbitals along edges, into faces or into cavities to obtain the required number of bonding orbitals. Furthermore, it can be a significant approximation to neglect mixing between the radial and tangential orbitals in some clusters.⁵³ The corresponding problem in TSH theory is the mixing of TSH σ - and π type cluster orbitals, which is readily quantified by simply transforming the results of any MO calculation into a TSH theory cluster orbital basis (see below).

Teo's topological approach also deserves mention in this section.⁵⁴ It combines Euler's theorem with the idea of an effective atomic number rule for each cluster vertex, but involves a rather arbitrary parameter whose purpose is to correct for the formation of multicenter bonds.

4.3 Tensor Surface Harmonic (TSH) Theory

Stone's TSH theory is framed within LCAO-MO theory, whose power was first demonstrated in the field of cluster chemistry by Longuet–Higgins and Roberts⁵⁵ in providing the first satisfactory analysis of icosahedral $B_{12}H_{12}^{2-}$. (*See also LCAO Approximation.*) Here, it is perhaps worth mentioning that the popular nomenclature for such species, that is, 'electron deficient', is a misnomer. Although there are certainly not enough valence electrons in the cluster for all the nearest-neighbor contacts to represent two-center, two-electron bonds, it is not the case that there are unoccupied bonding orbitals. On the contrary, all the bonding molecular orbitals are precisely filled, as we shall see. (*See also Electron Deficient Compound*).

The closest forerunner to TSH theory was due to Hoffmann, Ruedenberg, and Verkade.⁵⁶ These authors used spherical harmonics at the center of the cluster to generate linear combinations of orbitals with particular symmetry and nodal characteristics. The energy of these orbitals could then be estimated by the number of angular nodes in the parent spherical harmonic. For alkali metal clusters, one could actually produce the same answers for the symmetries of the bonding orbitals as for the spherical jellium model (above) or TSH theory. However, once again the method cannot work for systems, where p and d orbitals contribute to the bonding, because then there are valence orbitals that have intrinsic nodal planes containing the radius vector of the atom. Stone's principal contribution was to produce a remedy for this problem.⁵⁷

Let us first consider how the π molecular orbitals of linear and cyclic conjugated polyenes may be obtained by a descent-in-symmetry approach. If the electrons moved in an average nuclear potential, the corresponding free-particle wavefunctions would be the solutions of the Schrödinger equation for a particle-in-a-box and a particle-on-a-ring, respectively. These are, of course, just sine and cosine functions,12,27 and there are 'good' quantum numbers associated with the linear momentum and the angular momentum about the center of the ring, respectively. The corresponding linear combinations of p^{π} orbitals, which have the same transformation properties as the free-electron functions, are obtained by taking the coefficients to be the values of the latter functions evaluated at the atom positions.²⁷ In fact, if the boundary conditions are chosen appropriately, this procedure gives precisely the molecular orbitals of simple Hückel theory in both cases, as shown below. This result should not be taken to mean that TSH theory has its basis in Hückel theory. Rather, it is an illustration that the descentin-symmetry results from the free-electron problem may be a very useful guide to the true LCAO-MO wavefunctions.

For a conjugated linear polyene with n atoms, it is not hard to show²⁷ that the normalized Hückel wavefunctions are given by

$$\psi_m = \sqrt{\frac{2}{n+1}} \sum_t \mathbf{p}^{\pi}(t) \sin \frac{\pi t m}{n+1} \tag{3}$$

where $1 \le m \le n$ and $p^{\pi}(t)$ is the π orbital at atom t. The solutions of the Schrödinger equation for a free particle-in-abox of length L are

$$\psi_m = \sqrt{\frac{2}{L}} \sin \frac{\pi x m}{L} \tag{4}$$

where m > 0. The (unnormalized) coefficients for each p^{π} orbital in the expansion are now obtained from the values of $\sin \pi x m/L$ at the atom positions if we identify x/L with t/(n + 1). For a cyclic polyene, the normalized Hückel wavefunctions are

$$\psi_{ms} = \sqrt{\frac{2}{n}} \sum_{t} \mathbf{p}^{\pi}(t) \sin \frac{2\pi t m}{n} \quad \text{or}$$
$$\psi_{mc} = \sqrt{\frac{2}{n}} \sum_{t} \mathbf{p}^{\pi}(t) \cos \frac{2\pi t m}{n} \tag{5}$$

while for a free particle-on-a-ring the wavefunctions may be written as

$$\psi_{ms} = \sqrt{\frac{1}{\pi}} \sin m\phi \quad \text{and} \quad \psi_{mc} = \sqrt{\frac{1}{\pi}} \cos m\phi \tag{6}$$

where ϕ is the angle that describes the particle's position on the ring. In this case, we may obtain the expansion coefficient for $p^{\pi}(t)$ from the above functions by setting $\phi = 2\pi t/n$.

Stone applied similar reasoning to the problem of a three-dimensional cluster. Here, the solutions of the corresponding free-particle problem for an electron-on-asphere are spherical harmonics.¹² These functions should be familiar because they also describe the angular properties of atomic orbitals.²⁷ Two quantum numbers, L and M, are associated with the spherical harmonics, $Y_{LM}(\theta, \phi)$, and these define the eigenvalues for the operators \hat{L}^2 and \hat{L}_z , which correspond to the square of the total orbital angular momentum and its projection on the z-axis, respectively. It is more convenient to use the real linear combinations of $Y_{LM}(\theta, \phi)$ and $Y_{L-M}(\theta, \phi)$ (except when M = 0), and these are written as $Y_{LMc}(\theta, \phi)$ and $Y_{LMs}(\theta, \phi)$ because they are proportional to $\cos M\phi$ and $\sin M\phi$, respectively. Hence, the functions Y_{10} , Y_{11c} , and Y_{11s} are proportional to z, x, and y, respectively, as in p_z , p_x , and p_y atomic orbitals.

We now categorize the basis atomic orbitals in any, roughly spherical, cluster according to the number of nodal planes they possess that contain the radius vector. Hence, s atomic orbitals are classified as σ -type cluster orbitals, and so are p_z and d_{z^2} orbitals, where the local axes at each vertex are chosen with the *x* and *y* directions tangential to the surface of the sphere so that *z* points outwards along the radius vector. Radially directed hybrids, such as sp_z are also σ -type under this classification. Examples will be illustrated below. π -type cluster orbitals have one intrinsic nodal plane containing the radius vector, for example, p_x , p_y , d_{xz} and d_{yz} in the same axis system. d_{xy} and $d_{x^2-y^2}$ functions contain two such nodal planes, and are known as δ orbitals.^{27,57}

A set of σ -type atomic orbitals transform amongst themselves under point group operations like scalar quantities. Hence, to construct descent-in-symmetry-type LCAO cluster orbitals, we simply follow the same reasoning as for the linear and cyclic polyenes, above, and define (unnormalized) σ -type cluster orbitals as

$$L^{\sigma}_{\mu} = \sum_{t} Y_{L\mu}(\theta_{t}, \phi_{t})\sigma(t)$$
⁽⁷⁾

where $\mu = Mc$ or Ms, $\sigma(t)$ is a σ -type basis orbital at atom tand θ_t and ϕ_t are the angular coordinates of atom t. We write S, P, D, \ldots when $L = 0, 1, 2, \ldots$, by analogy with atomic orbitals. This is as it should be, for our assumption that the orbital angular momentum of an electron about the center of the cluster provides approximate quantum numbers is not unlike describing the cluster as a pseudoatom.

 σ -cluster orbitals transform like the parent spherical harmonics in any given point group, and these properties are easily determined from standard descent-in-symmetry tables.⁵⁸ Sometimes it may be more convenient to omit the μ subscripts from the cluster orbitals and give the transformation properties instead. For example, the six 2s orbitals in Li₆ form a basis for a representation that spans¹² $A_{1g} \oplus T_{1u} \oplus E_g$. When transforming to a basis of cluster orbitals, we generally start from functions with the smallest *L* and work up. In this case, the cluster orbitals are $S^{\sigma}(A_{1g})$, $P^{\sigma}(T_{1u})$, and $D_{0,2c}^{\sigma}(E_g)$ as illustrated in Figure 1, where the three $P^{\sigma}(T_{1u})$ functions transform like *x*, *y*, and *z* and correspond to the Y_{11c} , Y_{11s} , and Y_{10} spherical harmonics. Note that in this case, the energetic ordering is simply expected to follow the number of nodes in the cluster orbital.

 π -type basis functions, however, transform like a set of unit vectors because the intrinsic nodal plane in each one defines a particular direction. Stone recognized that appropriate LCAO combinations may be formed using vector surface harmonics, which have both magnitude and direction at any given point in space. Hence, instead of LCAO expansion coefficients, which are just the values of spherical harmonics evaluated at the atom sites, the coefficients for π -type basis functions define not only an amplitude but also the *direction* in which the π -functions point.^{27,57}



Figure 1 The (unnormalized) σ -cluster orbitals of an *Octahedral* cluster, such as Li₆ for which the basis functions are 2s orbitals.²⁷ The light and dark shading indicates the phase; the atoms are represented as small filled black circles. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)

In fact, two types of vector function can be derived from the spherical harmonics, and these are defined by

$$\mathbf{V}_{LM} = \nabla Y_{LM}$$
 and $\overline{V}_{LM} = \mathbf{r} \times \mathbf{V}_{LM} = \mathbf{r} \times \nabla Y_{LM}$ (8)

where \times denotes the vector cross product and ∇ is the gradient operator, which is $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$ in Cartesian coordinates. These vector functions are clearly orthogonal; V_{LM} has the same parity as the parent Y_{LM} ; it is a *polar* (or even) vector surface harmonic. \overline{V}_{LM} has the opposite parity (i.e. it changes sign under inversion if *L* is even, and is unchanged if *L* is odd) and is an *axial* (or odd) vector surface harmonic. The first π -cluster orbitals are the P^{π} and \overline{P}^{π} sets because the derivatives of $Y_{00}(\theta, \phi)$ are zero. We denote the even and odd sets generically by L^{π} and \overline{L}^{π} respectively; the p^{π} cluster orbitals of an octahedron are given in Figure 7.

Linear combinations of radial p orbitals, or sp hybrids, may be used to construct σ -cluster orbitals as mentioned above. If we consider an *n*-vertex cluster, then there are $2n \pi$ -type p orbitals, that is, two at each vertex, and these correspond to the two independent directions at each site tangential to the surface of the sphere upon which all the atoms are assumed to lie. It is convenient to choose the two directions corresponding to the spherical polar coordinates θ and ϕ increasing, that is, along the unit vectors $\hat{\mathbf{e}}_{\theta}$ and $\hat{\mathbf{e}}_{\phi}$. Using the standard form for the gradient vector operator in spherical polars, this gives the two orthogonal vector functions

$$\mathbf{V}_{L\mu} = \frac{\partial Y_{L\mu}}{\partial \theta} \hat{\mathbf{e}}_{\theta} + \frac{1}{\sin \theta} \frac{\partial Y_{L\mu}}{\partial \phi} \hat{\mathbf{e}}_{\phi} \quad \text{and}$$
$$\overline{\mathbf{V}}_{L\mu} = -\frac{1}{\sin \theta} \frac{\partial Y_{L\mu}}{\partial \phi} \hat{\mathbf{e}}_{\theta} + \frac{\partial Y_{L\mu}}{\partial \theta} \hat{\mathbf{e}}_{\phi} \tag{9}$$

The θ component of $\overline{\mathbf{V}}_{L\mu}$, written $\overline{V}_{L\mu}^{\theta}$, is the same as the negative of $V_{L\mu}^{\phi}$ while $\overline{V}_{L\mu}^{\phi} = V_{L\mu}^{\theta}$. Hence, odd π cluster orbitals may be obtained from their even partners by rotating the p orbital components through 90° about the radius vector. These cluster orbitals may be written as

$$L^{\pi}_{\mu} = \sum_{t} \left(V^{\theta}_{L\mu}(t) \mathbf{p}^{\theta}(t) + V^{\phi}_{L\mu}(t) \mathbf{p}^{\phi}(t) \right) \quad \text{and}$$
$$\overline{L}^{\pi}_{\mu} = \sum_{t} \left(\overline{V}^{\theta}_{L\mu}(t) \mathbf{p}^{\theta}(t) + \overline{V}^{\phi}_{L\mu}(t) \mathbf{p}^{\phi}(t) \right) \tag{10}$$

where the functions are evaluated at the atom positions *t* as for the σ cluster orbitals. We could therefore sketch the π cluster orbitals from p^{θ} and p^{ϕ} orbitals at each vertex using the appropriate expansion coefficients. However, an alternative representation would take just one resultant p orbital, which is the superposition of these two, taking into account their relative weights in a given cluster orbital. This is just the same as choosing one p orbital at each site with the direction and magnitude of the tangential component of $V_{L\mu}$ or $\overline{V}_{L\mu}$ at that point. This fact was used to produce Figure 7 in Section 5.

As for σ cluster orbitals, the transformation of basis to give π cluster orbitals from π -type basis atomic orbitals is not unique. To define a transformation, we must first form and reduce the representation, $\Gamma_{\pi/\overline{\pi}}$, spanned by the $2n \pi$ orbitals of a given *n*-vertex cluster.²⁷ Conventionally, we start from L = 1, M = 0 and take the corresponding L^{π}_{μ} and \overline{L}^{π}_{μ} cluster orbitals until we have matched the irreducible representations contained in $\Gamma_{\pi/\overline{\pi}}$ in number and type. Usually, this gives a linearly independent set of cluster orbitals; if not, then functions of higher L or M with the appropriate symmetry are substituted to produce such a set. It is helpful to realize that L^{π}_{μ} orbitals transform in the same way as the parent $Y_{L\mu}(\theta, \phi)$ functions under operations of the point group; the corresponding odd functions \overline{L}_{μ}^{π} transform in the same way under pure rotations, but with a sign change under reflections, inversions, and rotation-reflections.²⁷ Detailed worked examples for the equilateral triangle and the octahedron may be found elsewhere.27

Transition metal clusters also have d_{xy} and $d_{x^2-y^2}$ atomic orbitals, which are classified as δ -type in TSH theory. To represent the transformation properties of these orbitals, we use second derivatives of the spherical harmonics, that is, tensor spherical harmonics – hence the name of the theory. As for the vector surface harmonics, there are again both odd and even δ cluster orbitals, denoted by \overline{L}^{δ} and L^{δ} , respectively. Usually, both sets are completely filled in transition metal clusters, and we will not consider their properties in any detail in this review. However, the cases of partial occupation are important and have been described in previous articles.^{27,59}

Having provided an overview of the TSH theory cluster orbital transformation, it may be as well to emphasize once more the idea behind this approach, namely, to guess first approximations to the true molecular orbitals of the system. In this section, we have basically dealt with the mechanics of this transformation; to see how it leads to a general theoretical basis for structure-electron counting rules, we need to know the energies of the cluster orbitals. This problem is considered in the next section; for σ cluster orbitals, simple node-counting arguments suffice, while for clusters where π cluster orbitals are occupied, we must introduce the TSH theory 'pairing principle'.

There are, however, some other useful applications due to Mingos and coworkers that are based upon or framed within TSH theory, but will not be dealt with here. For example, the TSH theory pairing theorem may be generalized and used to analyze nonbonding orbitals in hydrocarbon polyenes, coordination compounds, and clusters.⁶⁰ The ligand and central atom valence orbitals may be classified using TSH theory to analyze the bonding and the stereochemistries of coordination compounds.⁶¹ Finally, an alternative transformation framework has been developed in terms of edge-localized and face-centered equivalent orbitals.⁶²

5 FURTHER DEVELOPMENT OF TSH THEORY

5.1 Clusters Involving Only σ orbitals

5.1.1 Characteristics of σ cluster Orbitals

In clusters where the contributions of p and d atomic orbitals can be neglected, the bonding is especially simple. In such cases, we need to only consider σ cluster orbitals, whose energies are basically defined by node counting. For such systems, the same qualitative energy-level pattern often results as for jellium models, because the angular parts of the jellium wavefunctions are also spherical harmonics. Hence, the same 'magic numbers' for precisely filled electronic shells are also found, as mentioned in Section 4.1 above. The σ cluster orbitals for an octahedron were illustrated in Figure 1.

For a cluster with *n* vertices, the cluster orbital transformation involves *n* functions. For deltahedral geometries, it is generally not necessary to use the cluster orbitals from the set with L + 1 until all the 2L + 1 members of the set based upon the spherical harmonics $Y_{L\mu}(\theta, \phi)$ have been used. However, this is not possible for all systems, such as three-connected structures and bipyramids.²⁷ For example, if all the atoms of a particular cluster happen to lie on nodal planes of one of the spherical harmonics, then no σ cluster orbital can be constructed from that function.

The energies of the L^{σ}_{μ} depend principally upon the value of L, because this defines the number of angular nodes. The nodeless S^{σ} orbital always lies lowest, followed by P^{σ} , D^{σ} , ..., and so forth. Furthermore, for a given value of L, the L^{σ} orbitals become more bonding as the number of atoms in the cluster increases, so long as all these atoms lie approximately on a single sphere.⁵⁷ The P^{σ} and D^{σ} orbitals usually become bonding when n is greater than about 6 and 16, respectively. Hence, filled bonding sets of orbitals are expected for 2 electrons, 8 electrons (n > 6), and 18 electrons (n > 16), and these correspond to the same 'magic numbers' for sodium clusters as predicted by the jellium model, above. However, in a finite cluster, the degeneracies associated with spherical symmetry are usually split, so this is by no means a complete explanation of why such magic number clusters are especially stable. Furthermore, one should really be more precise about whether it is kinetic or thermodynamic stability (or both) that is in question.

5.1.2 Splitting of σ cluster Orbitals

In radially bonded clusters, the bonding cluster orbital energy levels lie lower when the number of nearest neighbors per atom is maximized, and this usually corresponds to close-packed high-symmetry structures. However, in clusters that do not correspond to completely filled S^{σ} , P^{σ} and so on, shells, it may be more favorable for the cluster to distort and open up a significant *HOMO-LUMO* gap. The splittings induced by symmetry-lowering distortions of an L^{σ} shell follow an approximate center-of-gravity rule,⁶³ and so stabilization of the occupied orbitals and a large *HOMO-LUMO* gap are synonymous at this qualitative level of theory. The sense of the splitting (i.e. which orbitals are stabilized and which are destabilized) depends upon the way in which the cluster is distorted and can be analyzed rather like the splitting of atomic d orbitals in transition metal complexes.⁶⁴

Two different classes of distortion may be recognized, namely oblate and prolate.⁶³ A prolate molecule, like CH_3F , has two equal principal moments of inertia, which are greater than the third, while an oblate molecule, like NH_3 , has two equal moments of inertia, which are less than the third. In each case, the unique axis corresponds to a rotational axis of order 3 or more. The classification may be loosely extended to less symmetrical species, where two of the principal moments of inertia are similar and different from the third.

If applied with due caution, these ideas may provide useful insight. In any planar structure, the P_0^{σ} cluster orbital vanishes if the z axis is taken perpendicular to the plane, and we cannot apply the barycentre principle. In the triangle and square, the $P_{1c,1s}^{\sigma}$ orbitals are antibonding and nonbonding, respectively, and Na₃, Na₄, Li₃, Li₄ are all found to be planar, albeit relatively unsymmetrical, structures.¹¹ In nonplanar clusters with more than around 6 atoms, the $P_{1c,1s}^{\sigma}$ pair are expected to lie lower than P_0^{σ} , as shown in Figure 2. In agreement with this observation, both Na₆ and Li₆ exhibit a low-energy oblate geometry, that is, a capped pentagonal structure, as well as a planar raft, and both are favorable according to ab initio calculations.¹¹ In contrast, both Na₈ and Li₈ are calculated¹¹ to adopt tetracapped tetrahedral geometries, where the P^{σ} orbitals are all degenerate and precisely filled.

Similar considerations apply to gold clusters of the form $Au_m(PPh_3)_m^{x+}$, where the 5d orbitals may be treated as a closed shell in the first approximation, and bonding occurs principally through inwardly directed $s/p_z \sigma$ hybrids.⁶⁵ For example,

 P^{σ}_{0}



Figure 2 The idealized splitting of the P^{σ} orbitals in nonplanar oblate and prolate clusters



Figure 3 The gold skeletons of (a) $Au_6(PPh_3)_6^{2+}$ and (b) $Au_7(PPh_3)_7^+$

Au₆(PPh₃)₆²⁺ has a D_{2h} pseudoprolate gold skeleton, in which the P_0^{σ} cluster orbital is preferentially stabilized. However, Au₇(PPh₃)₇⁺ is an oblate pentagonal bipyramid, where the two $P_{1c,1s}^{\sigma}$ orbitals are occupied²⁷ (Figure 3).

5.2 The TSH Pairing Principle

In most clusters, the bonding is more complicated than for the systems discussed in the previous section, because π -cluster orbitals must be considered. One simplification is obtained from an energy-pairing relation⁵⁷ between even cluster orbitals L^{π}_{μ} and their odd partners \overline{L}^{π}_{μ} .

The idea of a pairing rule may be more familiar in the context of conjugated alternant hydrocarbons (which are defined as those containing no odd-membered rings). Coulson and Rushbrooke⁶⁶ showed that the Hückel molecular orbitals of such systems occur in pairs with energy $\alpha \pm \lambda\beta$, where α and β are the usual energetic parameters of *Hückel Theory*.¹² The LCAO coefficients of either of the partner orbitals may be obtained from the other by changing the signs of alternate coefficients.

The TSH theory pairing principle plays a similar role in cluster bonding. It can be shown that the energies of partner L^{π}_{μ} and \overline{L}^{π}_{μ} cluster orbitals have the same magnitude but opposite signs with respect to an origin at α . Several approximations are made in the proof,²⁷ for example, all the atoms are assumed to lie on a sphere, and the β parameters for π orbitals interacting in σ - and π -fashion are assumed to be the same. Neglect of nonnearest neighbors is not necessary, however.²⁷ The usefulness of this result is probably best illustrated by the detailed analysis of B₆H₆²⁻ in the following section.

5.3 Bonding in Deltahedral Clusters

5.3.1 Analysis of $B_6H_6^{2-}$

As mentioned in Section 3, the deltahedral *closo*-boranes, $B_n H_n^{2-}$, and carboranes, $C_2 B_{n-2} H_n$, have 4n + 2 valence

electrons. In this section, the presence of 2n + 1 bonding molecular orbitals, of which n + 1 may be identified with skeletal bonding, is explained using TSH theory. The structures of the *closo*-boranes from $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$ are illustrated in Figure 4 (*see also Boron: Polyhedral Carboranes*).

2n of the valence electrons are associated with *n* twocenter, two-electron B–H bonds, and will not be considered further. In deltahedra, we generally find that all the even π cluster orbitals are bonding in character, and all their odd partners are therefore antibonding, by the pairing principle. The n + 1 skeletal bonding orbitals may be formally identified as S^{σ} and the *n* even L^{π} orbitals. However, the P^{σ} set may be bonding in character too, but these orbitals transform in the same way as the corresponding P^{π} orbitals, and hence the two sets mix to give strongly bonding and antibonding combinations. Because of this σ/π mixing, we are generally guaranteed to have n + 1 skeletal bonding orbitals in deltahedral clusters.

A detailed analysis of the bonding in $B_6H_6^{2-}$ should help illustrate exactly how the TSH approach is applied; the labelling scheme for this cluster is illustrated in Figure 5. The six σ cluster orbitals, $S^{\sigma}(A_{1g})$, $P^{\sigma}(T_{1u})$, and $D^{\sigma}(E_g)$, generated by the s orbitals in Li₆ or Na₆ were shown in Figure 1. For $B_6H_6^{2-}$, it is more appropriate to form radial sp_z hybrids from the outset, and use these as the basis for the B–H bonds and the L^{σ} cluster orbitals. The same linear combinations are generated, and these are shown for the inwardly directed sets in Figure 6. Explicitly, the linear combinations are

Orbital	LCAO form	Energy
$S_0^{\sigma}(A_{1g})$	$\sqrt{\frac{1}{6}}(\sigma(1) + \sigma(2) + \sigma(3) + \sigma(4) + \sigma(5) + \sigma(6))$	$\alpha + 4\beta$
$P_{0,1c,1s}^{\sigma}(T_{1u})$	$ \begin{cases} \sqrt{\frac{1}{2}}(\sigma(1) - \sigma(6)) \\ \sqrt{\frac{1}{2}}(\sigma(2) - \sigma(4)) \\ \sqrt{\frac{1}{2}}(\sigma(3) - \sigma(5)) \end{cases} $	α
$D^{\sigma}_{0,2c}(E_g)$	$ \left\{ \begin{array}{l} \frac{1}{2}(\sigma(2) + \sigma(4) - \sigma(3) - \sigma(5)) \\ \sqrt{\frac{1}{12}}(2\sigma(1) + 2\sigma(6) - \sigma(2) \\ -\sigma(3) - \sigma(4) - \sigma(5)) \end{array} \right\} $	lpha-2eta

To form $P_{1c}^{\sigma} \equiv P_z^{\sigma}$, for example, we need only use the value of *z* at each vertex to obtain $P_z^{\sigma} \propto (\sigma(1) - \sigma(6))$. The energies have been evaluated in the Hückel approximation (*see Hückel Theory*), but this is simply to provide an idea of the bonding/antibonding character, and some more accurate calculations will be discussed below. (Note that the splitting obeys another center-of-gravity rule.) The normalization is simply $1/\sqrt{2}$, as overlap between the two σ orbitals has been neglected.²⁷



Figure 4 Structures of the *closo*-boranes from $B_5H_5^{2-}$ to $B_{12}H_{12}^{2-}$; these are the optimized geometries calculated with a minimal STO-3G basis. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)

To find the linear combinations required for the π cluster orbitals, we must first form and reduce the representation spanned by the 12 tangential p^{π} atomic orbitals, $\Gamma_{\pi/\pi}$. The result is²⁷ $\Gamma_{\pi/\pi} = T_{1u} \oplus T_{1g} \oplus T_{2g} \oplus T_{2u}$, and the corresponding cluster orbitals are $P^{\pi}(T_{1u})$, $\overline{P}^{\pi}(T_{1g})$, $D_{1c,1s,2s}^{\pi}(T_{2g})$, and $\overline{D}_{1c,1s,2s}^{\pi}(T_{2u})$. Owing to the particular



Figure 5 Structure and labeling scheme for the $B_6H_6^{2-}$ octahedron



Figure 6 Unnormalized L^{σ} cluster orbitals for $B_6H_6^{2-}$ formed from inwardly pointing sp_z hybrids. Each arrow represents a hybrid valence orbital contribution to the molecular orbital in both magnitude and direction. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)

symmetry of this cluster, it is quite convenient to express everything in Cartesian coordinates rather than spherical polars, that is, using p_x , p_y , and p_z instead of p^{θ} and p^{ϕ} . The only disadvantage is that the relationship between odd and even partner orbitals is more obvious when the latter basis functions are used, but this analysis may be found elsewhere.²⁷ In the following linear combinations, the *x*, *y* and *z* directions correspond to the global axes, as defined in Figure 5, not the local axes described previously. (Note that ∇z has no tangential components at vertices 1 and 6, and no radial components at the other atoms.) To form P_0^{π} , for example, we simply use the fact that $\nabla z = (0, 0, 1)$, so that $P_0^{\pi} = \frac{1}{2}(p_z(2) + p_z(3) + p_z(4) + p_z(5))$, where the normalization has been added as for the σ -cluster orbitals above. Hence, the full set of π orbitals is

Orbital	LCAO form	Energy
$P_{0,1c,1s}^{\pi}(T_{1u})$	$ \left\{ \begin{array}{l} \frac{1}{2}(p_{z}(2) + p_{z}(3) + p_{z}(4) + p_{z}(5)) \\ \frac{1}{2}(p_{x}(1) + p_{x}(6) + p_{x}(3) + p_{x}(5)) \\ \frac{1}{2}(p_{y}(1) + p_{y}(6) + p_{y}(2) + p_{y}(4)) \end{array} \right\} $	$\alpha + 2\beta$
$\overline{P}^{\pi}_{0,1c,1s}(T_{1g})$	$ \left\{ \begin{array}{l} \frac{1}{2}(-p_{y}(2)+p_{x}(3)+p_{y}(4)-p_{x}(5))\\ \frac{1}{2}(p_{y}(1)-p_{y}(6)-p_{z}(3)+p_{z}(5))\\ \frac{1}{2}(-p_{x}(1)+p_{x}(6)+p_{z}(2)-p_{z}(4)) \end{array} \right\} $	$\alpha - 2\beta$
$D_{1c,1s,2s}^{\pi}(T_{2g})$	$ \left\{ \begin{array}{l} \frac{1}{2}(p_x(1) - p_x(6) + p_z(2) - p_z(4)) \\ \frac{1}{2}(p_y(1) - p_y(6) - p_z(5) + p_z(3)) \\ \frac{1}{2}(p_y(2) - p_y(4) - p_x(5) + p_x(3)) \end{array} \right\} $	$\alpha + 2\beta$
$\overline{D}_{1c,1s,2s}^{\pi}(T_{2u})$	$ \left\{ \begin{array}{l} \frac{1}{2}(p_{y}(1) + p_{y}(6) - p_{y}(2) - p_{y}(4)) \\ \frac{1}{2}(-p_{x}(1) - p_{x}(6) + p_{x}(5) + p_{x}(3)) \\ \frac{1}{2}(p_{z}(2) + p_{z}(4) - p_{z}(5) - p_{z}(3)) \end{array} \right\} $	lpha-2eta

Again, the Hückel energies are given simply as a guide to the bonding character and do not imply that the Hückel approximation must necessarily be used. (*See also Hückel Theory*.) These functions are illustrated in Figure 7; note that all of them contain nodes, but where these are only intrinsic to the atomic orbitals, they do not lead to antibonding interactions. The intrinsic nodes are not explicitly illustrated; they would, of course, bisect each arrow.

A qualitative energy-level diagram for the separate L^{σ} and L^{π} sets is shown in Figure 8. When the two sets are allowed to mix, we expect to find seven strongly bonding orbitals that may be written as $S^{\sigma}(A_{1g})$, $P^{\sigma/\pi}(T_{1u})$ and $D^{\pi}(T_{2g})$. To verify this result, one may perform any sort of standard MO calculation and transform to the cluster orbital basis.²⁷ For comparison, the energy-level spectrum resulting from a minimal basis set calculation is given in Figure 9. This analysis illustrates the general result that *n*-vertex deltahedra have n + 1 skeletal bonding orbitals, which may formally be identified with the S^{σ} and L^{π} cluster orbitals. Although the composition of the occupied orbitals may change when σ/π mixing is admitted, the symmetries of the occupied set do not.

5.3.2 Symmetry-Forced Electron Count Deviations

We may also use the TSH formalism to explain systematic deviations from the usual deltahedral electron count. Such cases arise when the two members of a pair of degenerate L^{π} orbitals are paired with one another, and must therefore both be nonbonding.⁶⁷ This will be the case in any cluster where $\Gamma_{\pi/\pi}$ contains an odd number of *E*-type irreducible representations (IR's). Fowler⁶⁷ proved that any cluster with a rotation axis of order 3 or more, and a single vertex atom lying on that axis, would be forced to deviate from the usual skeletal electron count. These results were generalized by Johnston and Mingos,⁶⁸ who classified clusters as nonpolar, polar, or bipolar according to the number of atoms on the principal rotation axis, that is, 0, 1, or 2, respectively. For



Figure 7 L^{π} cluster orbitals for B₆H₆²⁻ formed from tangential p orbitals. Each arrow represents a p orbital contribution to the molecular orbital in both magnitude and direction, for example, all the arrow heads may be taken as the positive lobes. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)



Figure 8 Qualitative energy-level diagram for the L^{σ} and L^{π} cluster orbitals of an octahedron, prior to mixing. The units are arbitrary, and the relative scales for the σ (right) and π (left) sets cannot be determined precisely without further calculation. \overline{P}^{π} and \overline{D}^{π} both lie at +2 units and P^{π} and D^{π} at -2 units

polar deltahedral clusters, the principal axis can only have order 3, because all the faces must be triangular, and the



Figure 9 Energy-level diagram for $B_6H_6^{2-}$ calculated for the optimized geometry using a minimal STO-3G basis. The cluster orbitals have been picked out and labeled appropriately

axis passes through only one vertex, by definition. Hence, we expect deviations only for clusters with 3p + 1 vertices. In fact, axes of order 2 are possible for a polar deltahedron if an edge is bisected, as in $B_{11}H_{11}^{2-}$, and in such systems the HOMO-LUMO gap may be small, depending upon the splitting of the idealized *e* pair of frontier orbitals. When there is a threefold axis, the π orbitals of each set of three equivalent atoms span precisely two *E*-type IR's. However, the p^{π} orbitals of the unique vertex atom also span an E symmetry IR, giving 2p + 1 in total. Since all the even π cluster orbitals of E symmetry must find odd partners in this set, it follows that one pair must be paired with itself, and is therefore nonbonding⁶⁸ because of the energy-pairing principle described in Section 5.2. As this result depends critically upon the point group, it is hard to see how it could be derived by any other approach that does not consider symmetry explicitly.

Polar deltahedra with an approximately nonbonding e pair of orbitals might have either 4n or 4n + 4 valence electrons, depending upon whether these orbitals are vacant or fully occupied. Here, as usual, we are assuming that intermediate occupation numbers would be unfavorable, since they would entail open shells and/or Jahn–Teller distortions. Both cases are known for p = 1, that is, n = 4 vertices, with B₄Cl₄ and P₄ tetrahedra having 8 and 12 skeletal valence electrons, respectively. The latter cluster can also be described in terms of two-center, two-electron edge-localized bonds, as discussed below. Examples for larger systems are found amongst the hypothetical *closo*-boranes investigated by Fowler;⁶⁷some more complicated cases have also been considered and various examples are known for *Transition Metals*.^{69, 68}

In fact, it is also possible for nonpolar deltahedra to exhibit deviations from the usual electron-counting rules.⁶⁸ The D_{3h} tricapped trigonal prism provides an interesting example. In B₉H₉²⁻ (see Figure 4), which has the usual

n + 1 = 10 skeletal electron pairs, the HOMO is actually odd in character (\overline{F}_0^{π}) and the *HOMO-LUMO* gap is rather small. Hence, it is perhaps not surprising that B₉Cl₉ and Bi₉⁵⁺ have analogous structures, but 9 and 11 skeletal electron pairs, respectively.

5.3.3 The closo, nido, arachno Debor Pattern

TSH theory also provides an explanation for the number of bonding orbitals observed in related closo, nido, and arachno clusters.^{21,57} Consider the notional formation of a nido cluster by removing a B-H vertex from a closo system. Now assume an idealized axial symmetry for the cluster such that the p^{π} orbitals of the vertex removed span an E-type IR. If the original closo cluster has a 'normal' electron count, that is, n + 1 skeletal bonding orbitals, then it must have been bipolar, that is, there were two vertices lying on the rotation axis on different sides of the cluster. It follows that the nido cluster is itself polar, and could exhibit n or n + 2 skeletal electron pairs, where n is now the number of vertices remaining in the nido cluster. Furthermore, the approximately nonbonding e pair of orbitals must have significant amplitude around the open face, because they would interact strongly with the corresponding orbitals of the missing vertex. Usually, the open face is protonated, thus stabilizing the frontier e pair and leading to n + 2 occupied skeletal orbitals that is, the same as in the parent closo cluster with n + 1 vertices. The loss of just one inwardly directed σ hybrid does not generally destabilize the S^{σ} orbital significantly.

An alternative explanation has been given within the topological graph-theoretical framework⁵⁰ using the 'Principle of Polyhedral Excision'. Here, it is argued that the atoms bordering each 'hole' left by removing a vertex would interact to give a core-type bonding orbital in addition to the usual core orbital and the *n* bonding orbitals resulting from pairwise overlap of the tangential orbitals at each vertex. However, this does not explain the presence of a nonbonding pair of *e* orbitals around the open face, which can be verified by calculation.

Of course, as with all these general structure-electron count correlation 'rules,' there is scope for deviation. For example, if the nido cluster does not have a threefold or higher-order axis (a higher-order axis is possible because the cluster is no longer deltahedral), then the idealized e pair will be split. The electron count will then depend upon the splitting, specific stabilization by protonation, and so on. Of course, as successive vertices are removed, the cluster may also deviate significantly from the assumed roughly spherical arrangement of atoms.

The TSH formalism may also be used to explain the electron counts of arachno clusters, why the 'missing' vertex in a nido cluster usually gives the largest possible open face, and why it appears to be most favorable to 'remove' two adjacent vertices to give an arachno cluster. Since the (possibly idealized) nonbonding e pair of orbitals has

significant amplitude around the open face, each orbital must have a single nodal plane passing through this face. The consequent antibonding interactions are minimized if the open face is as large as possible, as then their contribution relative to the in-phase bonding interactions is minimized.⁵⁷ This also explains why neighboring vertices appear to be 'lost' to give arachno clusters. To rationalize the electron count of such an arachno cluster requires further idealizations.⁵⁷ The essential idea is that two *e*-type nonbonding pairs of orbitals are created; the details are omitted here.

5.4 Transition Metal Clusters

The analysis of these molecules is complicated by the presence of the d orbitals, which contribute one orbital of σ symmetry (d_{z^2} in local axes), two of π symmetry (d_{xz} and d_{yz}), and two of δ symmetry (d_{xy} and $d_{x^2-y^2}$). There are far more examples of deviations from the usual patterns in transition metal clusters than in main group clusters, and many of these must be treated specifically, although TSH theory may again provide a useful framework in which to perform the analysis. However, in this section the objective will simply be to understand the most common patterns, as set out in Section 3, which are typically found in clusters with π -acceptor ligands such as CO.

It is easiest to derive the number of inaccessible orbitals in this case, that is, the number of orbitals that are too high in energy to contain electrons, and we divide the *n*s, *n*p, and (n - 1)d orbitals (*n* here represents a principal quantum number, for example, 4s, 4p, 3d) into three sets. By suitable *Hybridization*, we may construct in-pointing and out-pointing σ and π orbitals, leaving one orbital of σ character and the two δ orbitals. The latter consist approximately of d_{z^2} , d_{xy} , and $d_{x^2-y^2}$, and are conveniently referred to as the ' t_{2g} ' set by analogy to the way they transform in *Octahedral* transition metal complexes. Similar divisions are made in the graph-theoretical approach.⁵¹

The t_{2g} set and the three out-pointing hybrids usually correlate formally with accessible orbitals, with varying ligand character, assuming that there are sufficient π -acceptor ligands to stabilize them. This is usually the case in clusters composed of so-called 'conical' M(CO)₃ vertices. However, deviations may occur for lower carbonyl to metal ratios. It follows that the detailed geometrical arrangement of the ligands is not of primary importance, so long as there are enough of them. This result is in agreement with the fluxionality commonly observed in transition metal carbonyls and with the view that the carbonyl arrangement is determined principally by packing considerations.⁷⁰ The remaining in-pointing σ and π orbitals then give rise to n+1 bonding and 2n-1antibonding orbitals, as discussed for main group deltahedral clusters in the preceding section. Indeed, this is actually the basis of the Isolobal Principle.²³ The antibonding orbitals are not stabilized by ligand interactions because they are inwardly directed, and hence they are termed 'inaccessible'. The result is 7n + 1 accessible orbitals and 14n + 2 valence electrons, in agreement with calculations by Lauher⁷¹ and Ciani and Sironi.⁷²

It is noteworthy that the δ orbitals are always considered to be accessible in this analysis, and need not be considered further. Of course, this assumption is not always true, but clusters where the δ orbitals need to be analyzed in detail will not be treated here.^{27,73} Furthermore, since the only inaccessible orbitals arise from the inwardly directed σ and π interactions, the same analysis for symmetry-forced electron counts involving one additional occupied (or unoccupied) orbital holds.⁶⁸ Closo, nido, and arachno relationships follow by analogy so long as no additional inaccessible orbitals arise.

5.5 Bonding in Three-Connected Clusters

Here, we deal with clusters such as prismane, C_6H_6 , and cubane C_8H_8 , which can simply be described in terms of edge-localized two-center, two-electron bonds. Why, then, is it necessary to devote any space to such molecules? The answer is that it was not initially clear how TSH theory can rationalize the electron counts of these molecules. Of course, this is not entirely surprising, as the *Hybridization* patterns used in the TSH model are not well adapted to cover this situation. However, the correct answer can be obtained without abandoning the framework developed in the preceding sections.

The reason why the TSH analysis of deltahedral clusters, with n + 1 skeletal bonding orbitals, is inapplicable is that the L^{π} and \overline{L}^{π} cluster orbitals are not necessarily bonding and antibonding, respectively, in three-connected clusters. This result is basically due to the low coordination number and the relatively sparse manner in which the vertices in three-connected structures cover a sphere.⁵²

An *n*-vertex three-connected cluster has 3n/2 edgelocalized bonds, that is, 3n skeletal valence electrons rather than the 2n + 2 found in deltahedra. Johnston and Mingos considered the 3n/2 skeletal bonding orbitals in terms of linear combinations of the localized bonds, identifying n/2 + 2combinations that are 'face-bonding' and n - 2 that are 'face-antibonding'.⁷⁴ The face-bonding combinations have all the localized bonds in phase around each face, the faceantibonding (or nonbonding) combinations do not, and lie somewhat higher in energy, though they are, of course, bonding overall. A TSH analysis^{52,74} identifies the n/2 + 2strongly bonding combinations as S^{σ} and n/2 + 1 members of the L^{π} set. The more weakly bonding skeletal orbitals then consist of the remaining n/2 - 1 L^{π} orbitals, and their parity-related \overline{L}^{π} partners.

5.6 Additional Examples

There is space to provide only a very brief mention of how TSH theory is able to rationalize some of the other bonding patterns mentioned in Section 3. TSH analyses of the bonding in cylindrical clusters⁷⁵ and the hyper–closo versus iso–closo discussion⁷⁶ may also be found in the literature.

5.6.1 Interstitial Atoms

For larger clusters, the central cavity may be big enough to accommodate additional atoms. For example, the distance from the shell to the center of a cuboctahedral cluster is the same as the nearest-neighbor distance within the shell, and the cavity at the center of an *Octahedral* transition metal cluster is typically large enough to accommodate first-row main group atoms such as boron, carbon, or nitrogen. The valence orbitals of such interstitial atoms will generally mix with inwardly directed L^{σ} and L^{π} orbitals of the shell that have the same symmetry, leading to strongly bonding and antibonding combinations.

For a main group atom in a radially bonded cluster (see Section 5.1), the analysis is especially simple, as the s and p orbitals of the interstitial transform in the same way as the S^{σ} and P^{σ} cluster orbitals. The net result is that the original energy-level spectrum is reinforced, with more strongly bonding s/S^{σ} and p/P^{σ} in-phase combinations and additional inaccessible antibonding combinations, as shown in Figure 10. Hence, the interstitial atom effectively acts as an electron donor, without producing any new bonding orbitals, and therefore represents a possible remedy for 'electron deficiency'. (See also Electron Deficient *Compound*.) However, this does not mean that a large charge is necessarily associated with the interstitial atom. A simple example is Na₆Mg in which the magnesium atom occupies the central position in a sodium octahedron. This cluster has 8 valence electrons, completely filling the bonding s/S^{σ} and p/P^{σ} orbitals.²⁷

The same pattern emerges in simple transition metal carbonyls²⁷ such as $Ru_6C(CO)_{16}^{2-}$, which has 86 valence electrons as does $Ru_6(CO)_{18}^{2-}$. Some more complicated



Figure 10 Schematic energy-level spectrum for a radially bonded cluster with a main group interstitial atom

examples²⁷ are provided by halide clusters with interstitial main group atoms, a wide variety of which have been characterized by Corbett and his coworkers.⁷⁷

5.6.2 The Capping,^{22,30} Condensation,³¹ and Inclusion⁷⁸ Principles

Of these three 'Principles' mentioned in Section 3, the Capping Principle is the easiest to understand.^{22,30} The others will only be mentioned briefly here; more details may be found elsewhere.²⁷It should also be mentioned that King has proposed alternative visualizations of the bonding in such systems within his graph-theoretical approach.⁵¹

Consider a transition metal cluster that consists of an n-vertex deltahedron with m additional caps that are well separated so that they do not interact significantly with one another. Because the inaccessible orbitals of the deltahedron are all inwardly hybridized, they will only mix very weakly with orbitals on the capping atoms, and we do not expect to obtain any new bonding orbitals in this fashion. If the caps are also transition metal atoms, then we may again describe each one in terms of three inwardly directed orbitals (one σ plus two π), a ' t_{2g} ' set and three outward-pointing hybrids (again one σ plus two π). The six orbitals consisting of the t_{2g} set and the outward-pointing hybrids will be accessible, but the inward-pointing hybrids mix with orbitals of the *n*-vertex deltahedron, which have already been formally identified as accessible. Hence, the addition of a single capping atom generally increases the valence electron count by just 12. However, additional accessible orbitals can occur if there are inwardly pointing \overline{L}^{π} orbitals generated by a set of capping atoms that are not matched in symmetry by any accessible orbitals of the inner sphere. The tricapped trigonal prism may be analyzed in this way.²⁷

5.6.3 Silicon Clusters

A short discussion of the bonding in small silicon clusters will demonstrate how the TSH framework may be useful in considering the structures of less familiar molecules. These species have received much attention in recent years, partly because of the technological significance of silicon as a semiconductor. Calculational strategies fall into two camps, namely, ab initio quantum mechanical treatments of some kind and analyses that employ analytic empirical atom–atom potentials.⁷⁹

Slee, Lin, and Mingos⁸⁰ have analyzed the geometries of small silicon clusters, exploiting a connection with the deltahedral boranes and carboranes. A silicon atom with an out-pointing lone pair and three in-pointing hybrids is isolobal to a B–H vertex. However, Si_n clusters have 4nvalence electrons, two fewer than the corresponding boranes, $B_n H_n^{2-}$. Hence, we should not expect the two series of clusters to be isostructural, but it may be helpful to start from the corresponding borane deltahedron and consider how the structure might distort to destabilize one of the skeletal bonding orbitals.⁸⁰ Of course, Si_n clusters could adopt structures analogous to C_n, with two-center, two-electron bonds and delocalized π systems. However, this is probably not favorable because carbon is unusual in its ability to form strong π bonds. Silicon clusters therefore tend to exhibit delocalized bonding and higher coordination numbers.

The $P_z^{\sigma/\pi}$ orbital, where the z-direction defines the principal rotation axis of the cluster, may be destabilized by contraction along this axis.⁸⁰ The D_{3h} minimum-energy structure found for Si₅ in ab initio calculations by Raghavachari⁸¹ may be viewed in this way as a squashed trigonal bipyramid. Alternatively, application of the Capping Principle discussed in the previous section shows that 2n skeletal electron pairs can also result through capping, and both Si₆ (capped trigonal bipyramid) and Si₁₀ (tetracapped octahedron or trigonal prism⁸²) appear to exploit this fact.

The empirical interatomic potentials cannot really account for the detailed geometries of clusters such as these, where the structure depends critically upon the molecular orbital spectrum. For example, a high binding energy has been predicted⁸³ for Si₁₃ in a centered icosahedral geometry. However, the 52 valence electrons in this cluster would require 12 lone pair orbitals and 14 skeletal bonding orbitals to accommodate them, whereas the centered icosahedron has only 13 skeletal bonding orbitals. A distortion is therefore predictable, although Si₁₃²⁺ might adopt a centered icosahedral geometry.

6 CLUSTER REARRANGEMENTS

Lipscomb⁸⁴ first proposed his diamond-square-diamond (DSD) mechanism for skeletal rearrangements in clusters in 1966, but in 1975 he commented that 'few reaction pathways in rearrangements of boron compounds are well understood'.⁸⁵ A general theory to rationalize the relative rearrangement rates of boranes and carboranes did not, in fact, emerge until 1987, when Wales and Stone⁸⁶ used TSH theory to deduce some orbital symmetry selection rules. An equivalent description was provided by Mingos and Johnston,⁸⁷ and subsequently the theory was further developed and various predictions made.⁸⁸ Combining the new theoretical tools provided by TSH theory with modern ab initio calculations now puts us in a significantly more optimistic position than in 1975.

In the DSD process (Figure 11), an edge common to two triangular faces breaks while a new edge is formed perpendicular to it. Hence, the idealized transition state geometry would have a square face. Degenerate rearrangements, in which the rearrangement leads to the same cluster skeleton, aside from possible permutations among atoms of the same element, are particularly important in small



Figure 11 Lipscomb's DSD process

clusters where there may only be one stable minimum-energy structure. The boranes, and associated carboranes, provide a good example. King89 used topological considerations to deduce which *closo*-boranes $B_n H_n^{2-}$ have geometrically possible single DSD processes available. If the connectivities of the vertices are α , β , γ , and δ , then a general DSD process may be written as $\alpha\beta(\gamma\delta)$, where the edge is broken between the vertices of connectivity α and β and made between the two with connectivities γ and δ .⁸⁹ For a degenerate single DSD process to be possible, there must therefore be vertices satisfying $\alpha + \beta = \gamma + \delta + 2$, and of the *closo*-boranes this condition is only satisfied for $B_5H_5^{2-}$, $B_8H_8^{2-}$, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$ (see Figure 4). However, of these four molecules only $B_8 H_8^{2-}$ and $B_{11} H_{11}^{2-}$ appear to be readily fluxional;⁸⁶ in the other two clusters, the geometrically feasible single DSD process turns out to be 'forbidden' by orbital symmetry.³³(See also Fluxional Molecule.)

Gimarc and Ott first noticed that the single DSD processes in $B_5H_5^{2-}$ and $B_9H_9^{2-}$ would result in crossings of filled and vacant molecular orbitals, and would therefore be expected to have high activation energy barriers.⁹⁰ (The hypothetical single DSD process in $B_5H_5^{2-}$ is, in fact, directly analogous to the *Berry Pseudorotation* in PCl₅.) Subsequent computational studies have confirmed the result⁹¹ for $B_5H_5^{2-}$ (and the corresponding carborane) and suggest that the orbital symmetry–'allowed' double DSD process may account^{92–93} for the experimental results obtained by Onak and coworkers for B, B'–disubstituted 2, $4-C_2B_5H_7$ derivatives.⁹⁴ Group theoretical analysis framed within TSH theory leads to two important theorems that enable orbital crossings to be easily identified:^{86,88}

- (1) A crossing occurs if the proposed transition state has a single atom lying on a principal rotation axis of order 3 or more.
- (2) A crossing also occurs if a mirror plane, which must pass through two atoms in the critical face, is retained throughout a DSD process.

Theorem 1 immediately reveals that the single DSD processes in $B_5H_5^{2-}$ and $B_9H_9^{2-}$ are forbidden. The result follows from the same considerations of nonbonding orbitals and symmetryforced deviations in electron count that were discussed in Section 5.3.2. The polar transition state in question must have a nonbonding *e* pair of *Frontier Orbitals*, which are absent in



Figure 12 Splitting of the frontier orbitals in the open face of a DSD transition state. One function is symmetric (S) with respect to the conserved mirror plane, the other is antisymmetric (A). Their energies change in opposite senses and lead to an orbital crossing

the starting and finishing structures, and therefore correspond to an orbital crossing.

Theorem 2 is a more subtle result of the TSH pairing principle, and may be deduced⁸⁸ by considering the number of occupied orbitals with a given parity under reflection. The frontier orbitals, which need not be strictly degenerate, are sketched in Figure 12. They have different parities under reflection through a mirror plane that includes either pair of opposite vertices. Hence, one orbital rises in energy and the other falls when the square face contracts along a diagonal, but the splitting is in the opposite sense for the other diagonal. If only a C_2 rotation axis is preserved throughout, then there is an avoided crossing, for the two frontier orbitals are both antisymmetric under this operation.⁸⁸

Using the above results, and the premiss that double DSD processes are less favorable than single DSD processes, and so on, (on the grounds that a single DSD process produces the smallest structural perturbation), Wales and Stone were able to rationalize the available experimental evidence for borane and carborane rearrangement rates.⁸⁶ The archetypal single DSD mechanism in $B_8H_8^{2-}$ has since been studied by accurate ab initio calculations⁹⁵ and is shown in Figure 13. Calculations for $C_2B_4H_6$ have also characterized a high-energy rearrangement mechanism based upon 'local bond rotation'.⁹⁶ The case of icosahedral $B_{12}H_{12}^{2-}$ and the associated carboranes (of which there are three isomers) is also interesting. There is no geometrically



Figure 13 Calculated reaction mechanism for $B_8H_8^{2-}$. The arrows superimposed upon the transition state represent appropriately scaled normal mode displacements for the mode with the unique imaginary frequency. Structures were selected along the reaction path so as to include all three stationary points plus three geometries at regular intervals on either side of the transition state. The structures were triangulated using distance cutoffs of 2.1 Å. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)

feasible single DSD process for this cluster, and earlier work⁸⁶ has shown that concerted hextuple and pentuple DSD processes are probably not responsible. Possible high-symmetry intermediates were investigated by Gimarc *et al.*,⁹⁷ but more recent results suggest that the interconversions probably occur via a complex series of rearrangements involving low-symmetry minima and transition states.⁹⁸ These pathways confirm previous suggestions made on the basis of orbital symmetry selection rules.⁸⁸ The highest barrier encountered on the pathway between the 1,2 and 1,7 carboranes involves a concerted double DSD process, as shown in Figure 14.

Of the other predictions concerning cluster rearrangement mechanisms using TSH theory, only one more will be mentioned here. This is the square-diamond, diamond-square (SDDS) mechanism that may occur in a cluster with a square face, such as square-based pyramidal $C_5H_5^+$. The TSH theory prediction is that a concerted mechanism should be orbital symmetry allowed if the edges that are made and broken lie in the same mirror plane. If one edge lies in a mirror plane and the other lies across it, then two crossings are predicted.^{27,88} The mechanism is unlikely to occur in *nido*-boranes, because of the additional bridging hydrogen atoms around the open face; however, recent ab initio calculations⁹⁵ have confirmed that it does indeed occur in $C_5H_5^+$, as shown in Figure 15.



Figure 14 Concerted double DSD process (calculated at the SCF level with an STO-3G minimal basis set) linking $1, 2-C_2B_{10}H_{12}$ with C_{2v} symmetry to a high-energy local minimum with C_s symmetry. The diagram is arranged as for Figure 13 except that the terminal hydrogen atoms are omitted for clarity and the distance cutoff for triangulation is 2.8 Å. The calculated barriers are 311 and 13 kJ mol⁻¹ for the forward and reverse processes, respectively. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)



Figure 15 The SDDS rearrangement of square-based pyramidal $C_5H_5^+$, which proceeds through a C_{2v} symmetry transition state.⁹⁵ The diagram is arranged as for Figure 13 and the triangulation cutoff is 2.1 Å. (This figure was produced using Mathematica 2.0 © Wolfram Research Inc., 1990.)

7 RELATED ARTICLES

Boron: Polyhedral Carboranes; Carbon: Fullerenes.

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