

Clusters in Inorganic and Molecular Beam Chemistry. Some Unifying Principles

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Clusters are ubiquitous in chemistry and physics, ranging from hydrocarbon polyhedra such as dodecahedrane¹ to transitory species found in molecular beams. The chemistry of interstellar space involves exotic carbon clusters,² and clusters of ions held in "traps" are of interest in plasma technology.³ Clusters are also important in the analysis of solid-state structures such as the Chevrel phases.⁴ To rationalize the unusual magnetic and electrical properties of the latter systems, it is natural to view the structures as extended arrays of interlinked clusters. In short, clusters are of great scientific interest in many fields, often because they grant us insights into the behavior of more complex systems at a relatively tractable level. Catalytic properties represent an outstanding example.⁵

Over the last few decades, great progress has been made in the theory of bonding in "inorganic" clusters such as boranes, carboranes, and transition-metal carbonyls. Most of these molecules are ligated, by hydrogen atoms or carbon monoxide, for example, but others, such as Sn_5^{2-} and Pb_5^{2-} , are not.⁶ Generally these species can be obtained in macroscopic quantities, and often their structures can be elucidated by X-ray crystallography. The most important patterns of electronic structure for these molecules are summarized in the Debor principle,⁷ polyhedral skeletal electron pair theory,⁸ and the isolobal principle.⁹ In the 1980s, Stone's tensor surface harmonic (TSH) theory has been used to provide a firmer theoretical foundation for these generalizations.¹⁰

Another area of cluster chemistry, which has tended to grow in isolation from "inorganic" cluster chemistry, involves clusters that may be formed in molecular

beams. Examples are alkali-metal,^{11,12} transition-metal,¹³ post-transition-metal,¹⁴ and silicon clusters.¹⁵ These species are usually only characterizable by mass spectroscopy and ab initio calculation (or, to some extent, electronic spectroscopy).

The jellium model involves a spherical approximation to the potential experienced by an independent electron in the field of all the nuclei and has been used to analyze the electronic structure of alkali-metal clusters. In fact, the jellium and linear combination of atomic orbitals (LCAO) methods lead to very similar results when only s orbitals are important. Furthermore, correlations between cluster shape and structure can also be analyzed within the same theoretical framework. Here we will review the relationship between the electronic structure of a cluster and its detailed geometry and show how some general principles apply to clusters from all branches of chemistry. The predictive value of these results will be especially important for molecular beam studies where structural information is so much harder to come by.

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The Jellium and Linear Combination of Atomic Orbitals Models

The peaks in an abundance spectrum of sodium clusters produced in a molecular beam have been rationalized by using the energy levels calculated for a one-electron central potential (a central potential is independent of the angular coordinates θ and ϕ).¹¹ In this *jellium model*, the precise details of the potential energy are "smeared out"; the calculated order of the energy levels for one such potential is¹¹

$$1s < 2p < 3d < 2s < 4f < 3p < 5g < 4d < 3s < 6h\dots$$

which is practically identical with the calculated levels for a free electron in a spherical box.¹⁶ The notation used is analogous to that for atomic orbitals, e.g., the 4d functions have two angular nodes and one radial node. Peaks are observed in the mass distribution of sodium clusters formed by supersonic expansion for 2, 8, 20, 34, 40, 58, and 92 atoms which correspond to filling up to the 1s, 2p, 2s, 4f, 3p, 5g, and 6h levels, respectively. Electronic shell structure of this kind has also been observed in extended Hückel calculations on lithium clusters.¹⁷

These results are linked to the success of Stone's tensor surface harmonic (TSH) theory, which has been used to treat the bonding in ligated clusters. In this approach, linear combinations of atomic orbitals (LCAOs) for a cluster with a single shell of atoms are formed from the wave functions for a free electron constrained to move on the surface of a sphere, i.e., the spherical harmonics.¹⁸ This method was inspired by the observation that the Hückel π orbitals for conjugated cyclic and linear polyenes can be constructed by using the wave functions for a free electron on a ring and in a box, respectively. The coefficients in the LCAO expansion are formed by evaluating the free-electron wave functions at the atom positions for the latter systems. For three-dimensional clusters, the problem is more complicated, but a similar rationale applies. The basis atomic orbitals are categorized as σ -, π -, or δ -type if they have 0, 1, or 2 nodal planes containing the radius vector of the atom, respectively. For a set of s orbitals, which are σ in character, we form a σ cluster orbital as

$$\psi_{L,\mu}^{\sigma} = \sum_t Y_{L,\mu}(\theta_t, \phi_t) \sigma(t) \quad (1)$$

where $\sigma(t)$ represents the s orbital at atom t , θ_t and ϕ_t are the angular coordinates of atom t , and $Y_{L,\mu}(\theta, \phi)$ is a real combination of spherical harmonics.¹⁰ The conventional shorthand for cluster orbitals based upon a particular spherical harmonic is L_{μ}^{λ} (or $\psi_{L,\mu}^{\lambda}$), where $\lambda = \sigma, \pi, \text{ or } \delta$ and $\mu = 0, 1c, 1s, \dots$ defines the value of M and whether a sine or cosine combination is taken. For example, the σ cluster orbitals of an octahedral cluster are $S^{\sigma}(a_{1g})$, $P^{\sigma}(t_{1u})$, and $D_{0,2c}^{\sigma}(e_g)$, as illustrated in Figure 1.

The object in forming approximate LCAO cluster orbitals is to diagonalize the Hamiltonian as far as possible. Hence the cluster orbitals should be symmetry

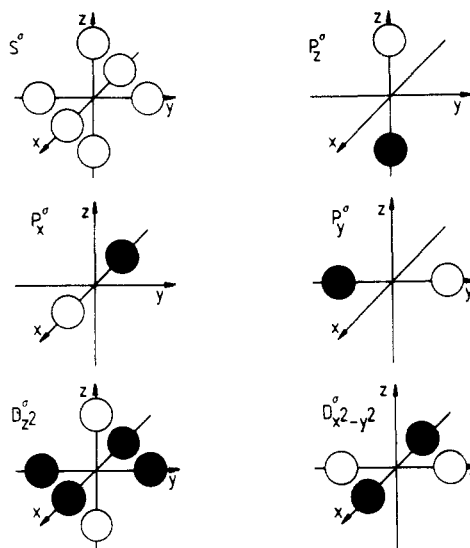


Figure 1. The σ cluster orbitals of an octahedral cluster such as Li_6 for which the basis functions are 2s orbitals.

adapted, and orbitals of the same symmetry species should mix as little as possible.¹⁹ The success of TSH theory²⁰⁻²² may therefore be traced to the fact that the orthogonality relations that hold for the parent free electron wave functions are still roughly true in a finite cluster.²³

For a cluster where only the valence s orbitals are important, the bonding is especially simple, and for a single shell of atoms, the TSH theory LCAO approach gives the same qualitative energy-level pattern as the jellium model. This is because any central jellium potential has wave functions for which the angular parts are simply spherical harmonics. To complete the comparison, we need to understand what happens when the cluster has several shells of atoms and when valence p orbitals must be included in the analysis.¹⁸

One way of approaching multispherical clusters is to consider the interactions between the TSH orbitals of different concentric spheres.²⁴ Alternatively, one may use a tensor solid harmonic theory which uses the eigenfunctions for the free electron in a sphere²⁵ to form the coefficients in an LCAO expansion just as the spherical harmonics alone were used for a single-shell cluster. The free-electron solutions in the latter case give the energy-level pattern set out at the beginning of this section.

The pronounced abundance of sodium cluster ions where closed electronic subshells are predicted for the neutral species requires further discussion. Since the actual clusters are not spherical, the $(2L + 1)$ -fold degeneracy of the free-electron wave functions must be broken. Why then are the nuclearities at which the free-electron electronic shells are closed still apparently so favorable? The answer is presumably that the splittings are small and that the favorable exchange

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energy associated with filled shells stabilizes such configurations. This implies that the nuclear potential experienced by the valence electrons in these alkali-metal clusters is well screened by the core electrons, in line with the usual description of bulk alkali metals. The lower lying orbitals based upon a particular set of free-electron wave functions are split less than those that are higher in energy, and for a given set of levels, the splitting decreases with increasing cluster nuclearity.

In a multishell cluster, the lower lying orbitals have greatest amplitude near the center of the cluster rather than the surface, and hence they are less influenced by surface effects. As more and more atoms are added to a cluster, the totally symmetric part of the electron-nucleus potential is progressively strengthened. Hence the low symmetry terms in the potential become relatively less important so long as the atoms are added in a reasonably regular manner. For orbitals with larger L quantum numbers, more of the nonspherical parts of the potential are important, and these levels experience greater splittings. Both trends may be discerned in the energy-level spectra of the *closo*-borohydrides.²⁵

These observations are important because they explain why simple free-electron-type electronic shell structure is not observed for main group or transition-metal clusters where the valence p (and d) functions must be considered. In this case, there are several electrons per vertex atom to accommodate, requiring relatively higher lying orbitals to be occupied which are more widely split by the details of the electron-nucleus potential. But this is not the only factor. In TSH theory, the radial and tangential p orbitals are separated and do not appear in the same cluster orbitals.²³ The tangential p orbitals transform like the components of a tangential vector, and hence their coefficients in an LCAO expansion are found by taking components of the gradient vector of a free-electron wave function.¹⁸ For a cluster with several shells of atoms, the appropriate free-electron wave functions for an electron in a spherical well are products of spherical harmonics and spherical Bessel functions, the latter containing all the radial dependence. The gradient of these functions has radial and tangential components, suggesting that our approximate LCAOs should contain both radial and tangential p orbitals.

To summarize: (1) A simple electronic shell structure is not expected for p (or d) orbitals because the coefficients in an approximate LCAO expansion of such orbitals must generally involve the derivatives of the free-electron wave functions rather than the wave functions themselves. When these orbitals play an important part in bonding, a central jellium model is inappropriate. (2) Clusters with several shells of atoms are different from those with single shells where the radial and tangential p orbitals can usually be separated to a good approximation. However, if only the s orbitals need to be considered, the electronic shell structure due to the vestigial $(2L + 1)$ -fold degeneracy of the spherical harmonics is still important. Note that the free-electron wave functions for any central potential, including the solutions to the particle on a sphere, particle in a sphere, and central jellium models, all contain spherical harmonics to describe the angular variation.

The main problem with any description of the bonding in multishell clusters is that no extra quantum

numbers (and hence no helpful orthogonality conditions) are associated with the radial dimension and the extra layers. Since we wish to diagonalize the Hamiltonian as far as possible by a judicious choice of wave functions, this is clearly unhelpful. Nonetheless, TSH theory generally provides a useful starting point for any such studies.

Radial Clusters: Shapes and Bonding

Radially bonded clusters are those in which only a set of orbitals with σ symmetry (i.e., with no nodal planes containing the radius vector of the atom) contribute to the bonding. The S^σ cluster orbital, with no angular nodes, is always the lowest in energy. P^σ orbitals, with a single nodal plane, only become bonding when $n > 6$, and the D^σ orbitals only become bonding when $n > 16$. The case of the $n = 6$ octahedron was illustrated in Figure 1. The S^σ , P^σ , and D^σ subshells are precisely filled in aufbau fashion at total electron counts of 2, 8, and 18, respectively. Here we are considering structures with only a single shell of atoms, so that there are no meaningful orbitals corresponding to jellium or hydrogenic functions with additional radial nodes such as 2s. Clusters with filled electronic L^σ shells have pseudospherical topologies, are more stable than the adjacent members of the series, and will in general have higher ionization potentials. Clusters with intermediate numbers of electrons generally adopt oblate or prolate geometries. (This effect has also been incorporated within a study of sodium clusters using a modified jellium model.²⁶) The change in geometry will be particularly favorable if it results in the opening up of a significant HOMO-LUMO gap.

Examples of prolate (like a rugby ball) and oblate (like a discus) clusters are provided by the trigonal bipyramid and the tricapped trigonal prism. The difference in geometry has important consequences for the splittings of the cluster orbitals in these molecules. For low-nuclearity clusters with more than about six atoms, the P^σ set is generally bonding while the D^σ set is antibonding and, therefore, splittings within the P^σ manifold are particularly important for defining ground-state properties.²²

The TSH theory cluster orbitals provide a clear explanation for these splittings; for example, in a prolate cluster, the P_0^σ orbital is stabilized relative to the $P_{\pm 1}^\sigma$ pair while the reverse is true for an oblate cluster. The splittings follow an approximate center-of-gravity rule such that the stabilization or destabilization of P_0^σ is roughly twice that of the $P_{\pm 1}^\sigma$ pair²² (Figure 2). The relevance of these arguments to real chemical situations can be appreciated by reference to gold and alkali-metal clusters. Sodium and lithium clusters have been observed in molecular beam experiments,^{11,12} and their structures have been studied by ab initio calculations^{27,28} (Figure 3). Both Na_8 and Li_8 are tetracapped tetrahedra, and the S^σ (a_1) and $P_{x,y,z}^\sigma$ (t_2) molecular orbitals accommodate a total of eight valence electrons to give a particularly favorable electronic configuration. In contrast, Na_6 and Li_6 , each with six valence electrons, are oblate with S^σ and two $P_{\pm 1}^\sigma$ orbitals of the P^σ set occupied, leading to a large HOMO-LUMO gap by

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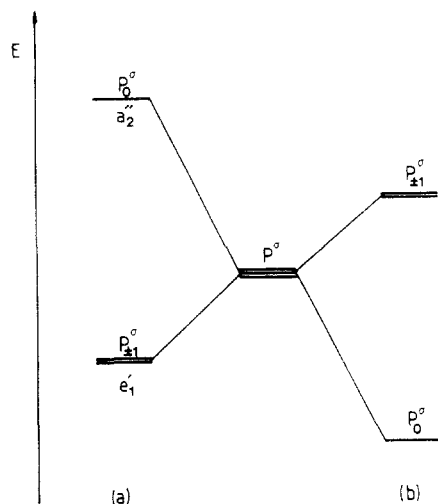


Figure 2. The splittings of the P^σ set for (a) oblate and (b) prolate geometries.

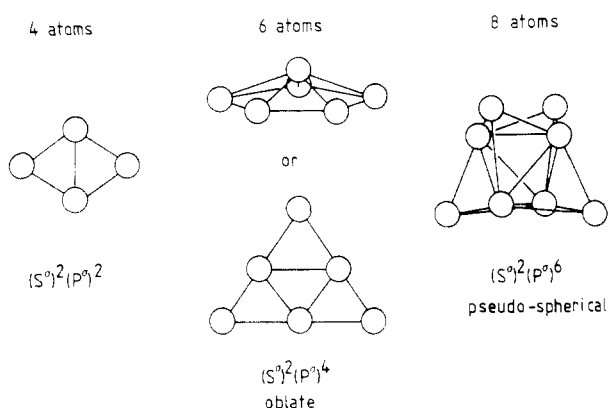


Figure 3. The calculated geometries of some sodium and lithium clusters.

destabilization of the P_0^σ component. An octahedral geometry would give an open shell configuration for these molecules. For Na_4 and Li_4 , each with four valence electrons, a diamond geometry is adopted in which one component of the P^σ set is uniquely stabilized (Figure 3).

The electronic structures of clusters with interstitial atoms can be understood similarly. The valence orbitals of the central atom have the same symmetry transformation properties as some of the σ cluster orbitals of the shell, and there are strong overlaps between the two sets. The s and p orbitals of an interstitial main group atom mix with S^σ and P^σ , respectively, and the resultant strong bonding interactions reinforce the bonding pattern of the parent cluster. Examples with eight valence electrons are Na_6Mg (octahedron) and Na_7Mg^+ (pentagonal bipyramid), which both have interstitial magnesium atoms.²⁷ If the cluster has a total of six valence electrons, then an oblate geometry is preferred: for Na_4Mg and Na_5Mg^+ , the ab initio calculated geometries are based on a square of sodium atoms and a planar pentagon of sodium atoms, respectively, with the magnesium atom at the center of each polygon. Similarly, MgNa_2 is linear, resulting in the stabilization of only one component of the P^σ set and producing the maximum possible stabilization for four valence electrons.

In contrast to the sodium and magnesium clusters described above, gold clusters can be isolated as air-stable crystalline solids; some examples are shown in

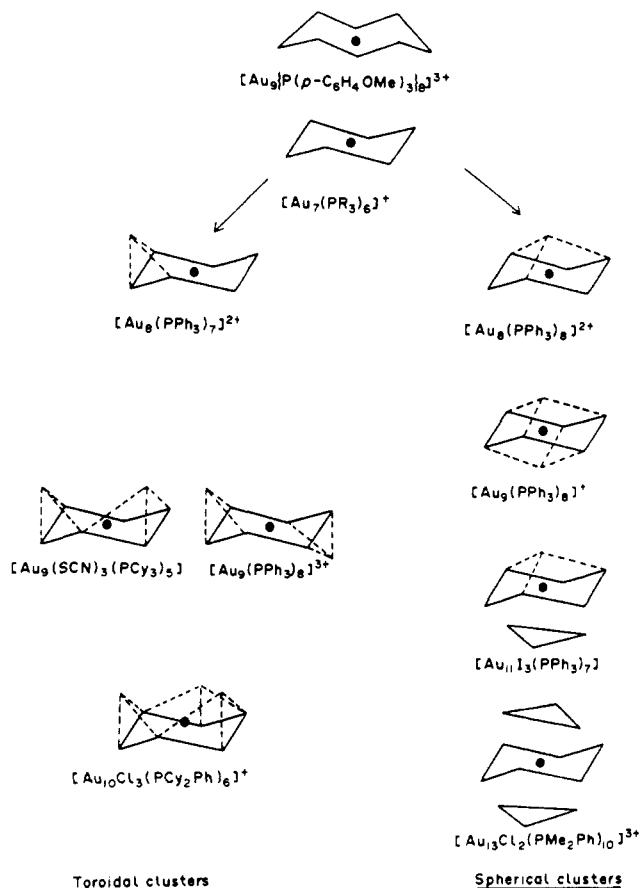


Figure 4. Pseudospherical and toroidal gold clusters.

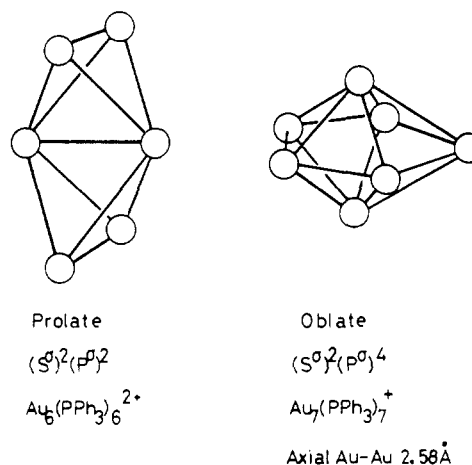


Figure 5. The gold skeletons of $\text{Au}_6(\text{PPh}_3)_6^{2+}$ (left) and $\text{Au}_7(\text{PPh}_3)_7^+$ (right).

Figure 4. Gold clusters with pseudospherical geometries have $12n_s + 18$ valence electrons, where n_s is the number of surface gold atoms. Each surface gold atom has a filled $5d$ shell and a bonding orbital associated with the Au- PPh_3 bond, thereby accounting for the $12n_s$ component in the above formula. The occupied skeletal molecular orbitals are S^σ , P^σ , and the $5d$ shell of the interstitial gold atom. A second class of gold clusters is described as toroidal because the peripheral gold atoms define a ring or torus; these species have $12n_s + 16$ valence electrons and are oblate so that the degeneracy of the P^σ cluster orbitals is split, with $P_{\pm 1}^\sigma$ being stabilized relative to P_0^σ .

$\text{Au}_6(\text{PPh}_3)_6^{2+}$ has a gold skeleton based on two tetrahedra sharing a common edge. This approximately

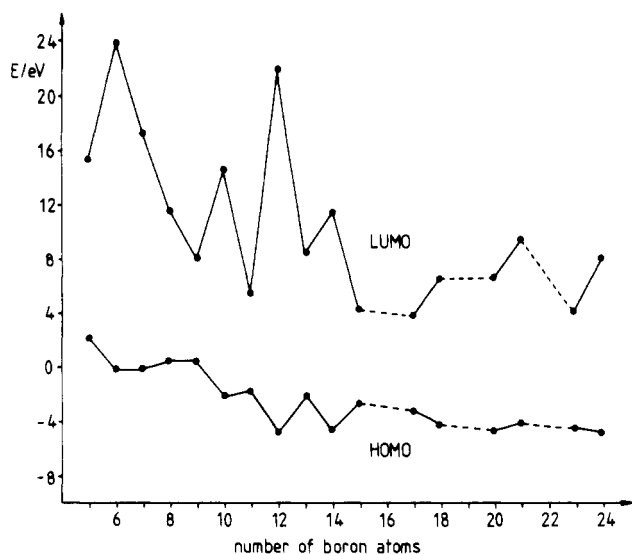
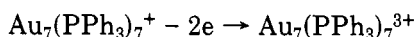


Figure 6. HOMO and LUMO energies (in electronvolts) for *closo*-boranes $B_nH_n^{2-}$ with n ranging between 5 and 24. Clusters with systematic deviations from $n + 1$ skeletal electron pairs are not included.

prolate geometry (Figure 5) leads to stabilization of P_0^σ at the expense of the other components of the P^σ manifold, and a favorable electronic configuration is achieved when four electrons occupy S^σ and P_0^σ . In contrast, $Au_7(PPh_3)_7^+$ is oblate (Figure 5), and the P^σ orbitals split so that P_0^σ is inaccessible. Clearly a capped octahedral geometry for $Au_7(PPh_3)_7^+$ is unfavorable for this electron count because it is prolate. However, the following electrochemical process should be accompanied by a change in cluster geometry:



oblate pentagonal bipyramid \rightarrow
prolate capped octahedron

Clusters Where π Orbitals Must Be Considered

Most clusters, such as the *closo*-boranes, $B_nH_n^{2-}$, are more complicated than the molecules discussed above because L^π orbitals must be considered. Fortunately the pattern that emerges can still be explained within the same theoretical framework.¹⁸ The $2n + 1$ valence electron pairs of $B_nH_n^{2-}$ reside in n B–H bonds and $n + 1$ additional *skeletal orbitals*. It transpires that the L^π orbitals may be divided into two equal sets, called even and odd, and that the n even orbitals are bonding while the n odd orbitals are antibonding. Hence the $n + 1$ occupied skeletal orbitals may be formally described as S^σ and the full set of even L^π orbitals.¹⁸ Although the P^σ set may be relatively bonding too, mixing with the P^π set gives bonding and antibonding combinations. In this section we give some illustrative examples for borohydrides, ions such as $Cs_3Pb_5^+$, silicon clusters, and nickel carbonyl clusters.

A plot of the HOMO and LUMO energies (calculated by using the Fenske–Hall method²⁹) for those clusters with $n + 1$ skeletal electron pairs is shown in Figure 6. Three factors are responsible for the trends observed in this figure, namely, the point group, nuclearity, and shape of the cluster.²² The first two factors both affect the degree of mixing between the various cluster orbitals. In clusters with high symmetry, the basis atomic

orbitals span a representation that will generally include a larger number of different irreducible representations than for a cluster of low symmetry. Hence, in low-symmetry molecules, the mixing of frontier orbitals with other orbitals of the same symmetry species raises the HOMO in energy and lowers the LUMO. For larger clusters, the increase in dimension of the basis set has the same effect.

The large HOMO–LUMO gaps observed for clusters of high symmetry, such as $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$, can be ascribed largely to factors one and two above. However, large gaps are also observed when the $L_{\pm 1}^\pi$ members only of the outer L^π manifold (the one with the largest L) are occupied, for example, in $B_5H_5^{2-}$ and $B_{10}H_{10}^{2-}$. Clusters with only a single member of the outer L^π set unoccupied also have relatively large gaps; for example, $B_7H_7^{2-}$ ($D_{\pm 1}^\pi$ and $D_{\pm 2}^\pi$ occupied) and $B_{16}H_{16}^{2-}$ ($F_{\pm 1}^\pi$, $F_{\pm 2}^\pi$, and $F_{\pm 3}^\pi$ occupied). These observations all suggest a splitting pattern with a high-lying L_0^π .²²

The wide applicability of TSH theory is further demonstrated by the exceptional stability of the $Cs_3Pb_5^+$, $Cs_3Sn_5^+$, and $Cs_3Sb_9^+$ ions observed by Martin in the gas phase.³⁰ These species are all isoelectronic to Zintl ions of the type Sn_5^{2-} , Pb_5^{2-} , Pb_9^{4-} , Bi_9^{5+} , and Ge_9^{4-} , whose structures are readily understood through TSH theory.²⁵ Presumably the isoelectronic ions have isostructural cluster skeletons. The same principles can be applied to series of mixed group 14/group 15 clusters such as $Sn_2Bi_3^+$, $Pb_2Sb_3^+$, Sn_3Bi_2 , Pb_3Sb_2 , Sn_3As_2 , Pb_3As_2 , Sn_5Bi_4 , Pb_5Sb_4 , and Sn_5As_4 , which have also been observed in the gas phase.¹⁴

A silicon atom with an out-pointing lone pair and three in-pointing skeletal hybrids is isolobal to a B–H vertex in a borane. However, an Si_n cluster has $2n$ pairs of valence electrons, so if there are n lone pairs, there can only be n skeletal electron pairs. Hence Si_n is not isostructural to $B_nH_n^{2-}$, and ab initio calculations indicate that the Si_n structures are also quite different from the chains and rings found for smaller carbon clusters.³¹ This difference arises because p^π bonds are unusually strong for carbon. Silicon, in contrast, has more diffuse 3p valence orbitals which overlap better in σ fashion. Hence the ab initio calculated geometries involve silicon clusters with high connectivities where the opportunity for p^π -type overlap is greater.

However, coordination number is not the only factor. The cluster must also have $2n$ low-lying molecular orbitals separated from the the unoccupied set by an appreciable gap. It is helpful to think in terms of the usual electron counting rules for boranes with $n + 1$ occupied skeletal orbitals, and then consider distortions which would lead to one of these becoming inaccessible. In particular, oblate geometries can lead to the destabilization of the P_z^π/P_z^σ orbital, and such a distortion does indeed occur in some of the lower nuclearity silicon clusters. The corresponding term in the potential energy transforms like $Y_{2,0}$ or $(3z^2 - r^2)/2$, which can affect the energies of the P_z^π orbitals significantly.^{22,32} Capping can also lead to structures with $2n$ low-lying orbitals; both Si_6 and Si_{10} adopt capped geometries.

Our final example involves the interpretation of some experimental results for nickel carbonyl clusters.¹³

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When size-selected Ni_n^+ ions react with carbon monoxide in the gas phase, three series of products are obtained: $\text{Ni}_n(\text{CO})_k^+$, $\text{Ni}_n\text{C}(\text{CO})_l^+$, and $\text{Ni}_{n-1}(\text{CO})_m^+$. The limiting values of k , l , and m for different values of n may be used to deduce candidate structures for the nickel skeletons in these systems by using the same theoretical framework as we have employed above.³³ We find that schemes based on successive face capping of a pentagonal bipyramid are in agreement with the results for all three series of clusters.³³ The face-capping scheme also leads naturally to a centered icosahedral nickel skeleton for $n = 13$ and gives a prime example of the importance of our theoretical framework for elucidating real chemical problems.

Concluding Remarks

Our aim in this Account has been to show how some unifying principles may be applied to understand the shapes and structures of clusters from diverse branches of chemistry. Throughout we have employed relatively straightforward ideas from Stone's symmetry-based

tensor surface harmonic (TSH) theory. The successes of the jellium model for alkali-metal clusters are intimately linked to the success of TSH theory, and the limits of applicability of the former model can be deduced from the latter. Small radially bonded clusters such as those of alkali metals and gold provide the simplest test of our approach. The structures of many such molecules can be rationalized by considering the splitting of the P^σ cluster orbitals in oblate and prolate geometries. Boranes and silicon clusters are more complicated because all the valence p atomic orbitals must be considered. However, we are still able to understand various properties of molecules ranging from borohydrides to metal carbonyls within the same framework. Thus we have demonstrated how the symmetry-based TSH formalism may be used to provide rapid, qualitative answers to questions of direct chemical importance. In many ways this approach is as useful in cluster chemistry as Hückel theory is in the study of π systems in organic molecules.

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