$(bpy)_2(CO)H]^0$ has an enhanced susceptibility toward insertion by CO_2. These electronic influences lie at the heart of the reactivity of these complexes. When combined with the ability to re-form the metal–hydride bond, they provide the mechanistic basis for the electrocatalyzed reduction of CO_2.

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Closed-Shell Electronic Requirements for Condensed Clusters of the Group 11 Elements

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The bondings in two limiting types of spherical gold clusters are considered in this paper. Close-packed spherical gold clusters form molecular orbitals that can be analyzed by using the jellium model. Closed shells correspond to the filling of the following wave functions: 1s, 1p, 1d, 2s, 1f, 2p, 1g, etc., which have been defined with pseudospherical symmetry labels. In the more open structures based on vertex-linked icosahedra, the molecular orbitals correspond to the summation of the S^σ and P^σ molecular orbitals associated with each icosahedron. Therefore, the closed-shell requirements correspond to $8n_p$ electrons, where n_p = the number of icosahedra. These closed shells result because the orbital interactions between icosahedra are much smaller than those within a single icosahedron. The more open linked icosahedral packing mode results in a greater utilization of electrons per gold atom than the more densely packed structures. The jellium analysis appears to be appropriate for describing the closed-shell requirements for gold clusters that have been studied in molecular beams but fails when applied to vertex-shared icosahedra. The closed-shell configurations of the latter are, however, satisfactorily analyzed by using the additive model based on the bonding requirements of the individual icosahedra.

Introduction

Molecular clusters, which can be either bare in molecular beam experiments or ligated in solid-state and solution experiments, have attracted considerable interest recently.[1] A jellium model has been developed to account for the electronic structures of bare clusters produced in molecular beams.[2] This model has successfully predicted several of the magic numbers in mass spectral data for alkali-metal clusters by associating their nuclearities with closed-shell electronic configurations for a particle in a sphere model. A crystal field perturbation analysis, which has been described as a structural jellium model, has led to the conclusion that alkali-metal clusters with closed-shell electronic configurations based on the jellium model adopt, when possible, high-symmetry (T_d, O_h, or I_h point group) structures based on close-packed or nearly close-packed spherical geometries.[3] It has also been demonstrated that the jellium model is closely related to the tensor surface harmonic theory[4] developed for transition-metal and main-group clusters.[5]

Ligated clusters provide some examples of these close-packed situations, but also less symmetrical clusters based on vertex, edge, and face sharings. In their formation, kinetic effects associated with the inertness of the metal–ligand bonds lead to the adoption of these more open metal structures in preference to close-packed arrangements. The closed-shell requirements of these clusters are well established through the polyhedral skeletal electron pair theory (PSEPT),[6] which provides relationships between the skeletal structure and the total number of valence electrons in the cluster. The tensor surface harmonic theory[4] provides a theoretical jus-

tification for these structural relationships. Other approaches to cluster bonding have been proposed by King[7] and Teo.[8] These simple rules, however, do not work well for metal clusters derived from s^1 configuration metals (e.g. alkali and group 11 metals), e.g. for Au and Ag ligated clusters.

The detailed understanding of the electronic structures in gold ligated clusters has been limited to those clusters of the type $[(AuPR_3)_n]^{x+}$ (n = 4–7)[9] and the centered clusters $[Au(AuPR_3)_n]^{x+}$ (n = 8–12).[10] In the former, the Au atoms are located approximately on a single sphere, whereas the latter have one Au atom in the center. It has been demonstrated that the bonding in these gold cluster compounds can be described in terms of the interactions between radially hybridized (s–z) orbitals of the AuPR$_3$ fragments. The following closed-shell requirements have been derived from extended Hückel molecular orbital calculations and the tensor surface harmonic theory (TSH):[4]

	tot. no. of valence electrons	no. of metal s electrons	
$[Au(AuPR_3)_n]^{x+}$	$12n + 18$	8	if the n surface gold atoms lie approximately on a sphere
	$12n + 16$	6	if the surface gold atoms adopt a toroidal or elliptical arrangement
$[(AuPR_3)_n]^{x+}$	$12n + 2$	2	spherical geometry
	$12n + 4$	4	prolate geometry
	$12n + 6$	6	oblate geometry
	$12n + 8$	8	spherical geometry

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The structural relationships can be expressed in terms of either the total number of valence electrons or the number of s valence electrons contributed by the individual gold atoms. The latter are particularly useful when more than one metal–ligand bond is associated with one or more of gold atoms because there are either additional phosphine ligands or bridging ligands. For example, both $[Au_4(PR_3)_4]^{2+}$ and $[Au_4(PR_3)_4I_2]$ have tetrahedral geometries consistent with the presence of two valence electrons derived from the gold 6s orbitals occupying an S^σ skeletal molecular orbital but have different numbers of metal–ligand bonds.

Although the d orbitals in gold clusters overlap significantly to develop a band that has a significant width for large clusters,[11] the closed-shell requirements of those clusters, which have been studied to date either in molecular beams or by molecular chemists, are determined primarily by the molecular orbitals resulting from the overlap of the gold 6s orbitals.

The spherical–prolate–oblate–spherical structural patterns observed in gold clusters have their counterparts in alkali-metal clusters.[12] Clemenger[13] was the first to highlight these structural distortions for alkali-metal clustes by introducing a modification to the jellium model.

In recent years, several condensed high-nuclearity gold cluster compounds that consist of two, three, and four icosahedra sharing vertices have been elegantly synthesized by Teo.[14–16] The closed-shell requirements of these condensed clusters cannot be simply interpreted by using the electron-counting generalizations given above. In addition, the jellium model[2] does not successfully account for their electronic structures. In this paper, we explore the closed-shell requirements of these condensed clusters and explore the relationship between the tensor surface harmonic and jellium models.

Results and Discussion

High-nuclearity clusters can be derived from the condensation of small polyhedra, e.g. tetrahedra or octahedra. However, for gold clusters, tetrahedral and octahedral clusters are relatively labile and cannot be readily isolated unless the steric requirements of the ligands prevent their aggregation. For (triphenylphosphine)gold clusters, the most stable geometries are generally based on centered clusters derived from the icosahedron with 8–12 surface gold atoms. Therefore, it is not sensible to describe a high-nuclearity gold cluster on the basis of vertex-sharing small polyhedra. A centered icosahedron of gold atoms is found at the upper limit of this range and, if associated with ligands with the appropriate cone angles, represents a very stable structure if associated with 162 valence electrons ($12n_s + 18$, n_s = number of surface gold atoms), e.g. $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$.[17] If the d electrons and the metal–ligand bonds are ignored, this corresponds to 8 valence electrons derived from the gold 6s orbitals.

Most higher nuclearity ligated gold and silver clusters adopt solid-state structures via the condensation of icosahedra through shared vertices. Therefore, Teo has proposed a series of highly symmetric supraclusters that are built of vertex-shared icosahedra.[18] These are S_2 (line), S_3 (triangle), S_4 (tetrahedron), S_5 (trigonal bipyramid), S_7 (pentagonal bipyramid), and S_{12} (icosahedron). Recently, Fackler et al.[19] proposed an alternative geometry for an Au_{67} cluster. We have reexamined in a systematic

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Table I. Description of Spherical Supraclusters Based on Vertex-Shared Icosahedra in Terms of Concentric Polyspheres

supracluster	no. of atoms in successive shells of concentric spheres	tot. no. of metal s valence electrons for a closed-shell config
linear dimer (M_{25})	1:10:2:10:2	16
planar triangle (M_{36})	3:6:3:12:12	24
tetrahedron (M_{46})[a]	6:4:12:12:12	32
trigonal bipyramid (M_{56})	9:5:18:12:12	40
planar pentagon (M_{61})[b]	1:10:5:5:20:10:10	40 + 6
pentagonal bipyramid (M_{75})[c]	1:10:5:7:30:10:12	56
pentagonal antiprism (M_{111})[d]	1:10:30:10:50:10	80 + 6
icosahedron (M_{127})	1:12:30:12:60:12	104

[a] Related clusters based on mono-edge-capped and edge-shared tetrahedra have M_{57} and M_{67}. [b] This arrangement has an additional atom encapsulated at the center of this pentagon; M_{60} is the cluster without this atom. An additional six metal s valence electrons (corresponding to the occupations of S^σ, P^σ_x, and P^σ_y) are associated with this central atom since a toroidal arrangement is adopted around it. [c] A pentagonal pyramid with a loss of the centered atom corresponds to M_{68}. [d] Same argument as in footnote b.

Table II. Description of Alkali-Metal Clusters Based on Fcc Closed Packing in Terms of Concentric Polyspheres[a]

alkali-metal or group 11 cluster point group with "magic number"		no. of atoms in successive shells of concentric spheres
M_8	T_d	4:4
M_{20}	T_d	4:12:4
M_{40}	T_d	4:12:12:12
M_{58}	T_d	4:12:12:12:12:6
M_{92}	T_d	6:8:24:12:12:6:12:12
M_9^+	O_h	1:8
M_{19}^+	O_h	1:12:6
M_{21}^+	O_h	1:12:8
M_{35}^+	T_d	1:12:6:12:4
M_{41}^+	T_d	1:12:6:12:6:4
M_{93}^+	O_h	1:12:6:24:12:24:8:6

[a] Illustrations of these structures are given in ref 21.

fashion the geometric requirements for the linking of icosahedra through their vertices, and the results are summarized in Table I.

This systematic approach to the condensation of icosahedra to form supraclusters encompasses the geometries proposed by Teo[18] and Fackler.[19] These authors have also provided photographs of these structures. One remark[18b] has to be made on the composition of the pentagonal-bipyramidal structure, M_{75} (S_7 in Teo's nomenclature), which is not M_{76}. This is because of the close approach of the two apical icosahedra resulting in an additional shared vertex instead of two atoms.

Although these clusters are not close-packed, they are approximately spherical and have high symmetries. They can be described as polyspherical clusters with the shell occupations summarized in Table I. These shell occupations are different from those in close-packed structures, where generally one does not observe successive layers having low densities.

The shell occupations for high-symmetry fcc structures are summarized in Table II. Therefore, gold clusters can form two major series of clusters which both have approximately spherical distributions of atoms but very different packing densities. The structures described above based on icosahedra with shared vertices are less densely packed than alternative spherical packing arrangements based on hexagonal, cubic, and icosahedral geometries, where the coordination numbers of more of the inner atoms are 12. In the following section, the closed-shell electronic requirements of the different packing modes are discussed and shown to be quite different. This may be an important property, since closed-packed and icosahedrally based structures have been proposed for high-nuclearity gold clusters.

Table III. Closed-Shell Requirement for the Supraclusters Based on Vertex-Shared Icosahedra According to the Jellium Model

supracluster	predicted formula for jellium model	config according to jellium model	predicted formula for this paper	config according to this paper[a]
linear dimer	$(M_{25})^{5+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2$	$(M_{25})^{9+}$	$2\times[(S^\sigma)^2(P^\sigma)^6]$
planar triangle	$(M_{36})^{2+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}$	$(M_{36})^{12+}$	$3\times[(S^\sigma)^2(P^\sigma)^6]$
tetrahedron	$(M_{46})^{6+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6$	$(M_{46})^{14+}$	$4\times[(S^\sigma)^2(P^\sigma)^6]$
trigonal bipyramid	$(M_{56})^{2-}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6(1g)^{18}$	$(M_{56})^{16+}$	$5\times[(S^\sigma)^2(P^\sigma)^6]$
planar pentagon	$(M_{61})^{3+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6(1g)^{18}$	$(M_{61})^{15+}$	$5\times[(S^\sigma)^2(P^\sigma)^6] + (S^\sigma)^2(P^\sigma_x,P^\sigma_y)^4$
pentagonal bipyramid	$(M_{75})^{5+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6(1g)^{18}(2d)^{10}(3s)^2$	$(M_{75})^{19+}$	$7\times[(S^\sigma)^2(P^\sigma)^6]$
pentagonal antiprism	$(M_{111})^-$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6(1g)^{18}(2d)^{10}(3s)^2(1h)^{22}(2f)^{14}(3p)^6$	$(M_{111})^{25+}$	$10\times[(S^\sigma)^2(P^\sigma)^6] + (S^\sigma)^2(P^\sigma_x,P^\sigma_y)^4$
icosahedron	$(M_{127})^{15+}$	$(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}(2p)^6(1g)^{18}(2d)^{10}(3s)^2(1h)^{22}(2f)^{14}(3p)^6$	$(M_{127})^{23+}$	$13\times[(S^\sigma)^2(P^\sigma)^6]$

[a] See Table I.
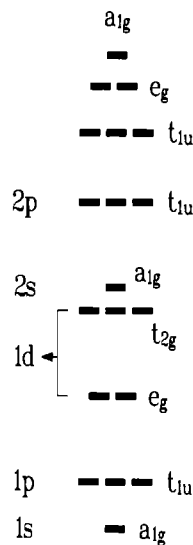
Figure 1. MO energy level diagram for an M_{19} metal cluster based on an fcc arrangement with O_h point group (s model used in the calculation).

Clusters with Jellium Closed-Shell Electronic Structures. Gold clusters that have closed-packed spherical structures conform to the jellium model. The observed "magic numbers" for Au_n^+, Ag_n^+, and Cu_n^+ bare clusters by the bombardment of the metals by Xe ions occur at $n = 3, 9, 21, 35, 41, 59, 93, 139,$ and $199.$[20] The jellium free-electron particle in a sphere model[2] predicts the following solutions to the Schrodinger equation: $1s < 1p < 1d < 2s < 1f < 2p < 1g < 2d < 3s < 1h.$ Closed-shell electronic structures are associated with the following total numbers of valence electrons: 2, 8, 18, 20, 34, 40, 58, 68, 70, 92, 138, 198, etc. These results suggest that the d shells of these atoms do not make a significant contribution to the definition of the closed shells, since they are very similar to those reported earlier for alkali-metal clusters.[2] In a previous paper,[21] we have described high-symmetry close-packed structures that are able to satisfy simultaneously the necessary closed-shell electronic and geometric requirements. The symmetries and numbers of atoms on successive spherical shells in these clusters are summarized in Table II. Illustrations of some of these structures have been given in our previous paper.[21] Extended Hückel molecular orbital calculations on gold clusters at the lower end of this series have confirmed the occurrence of these closed shells within an LCAO molecular orbital framework. The calculations were performed by using the methods and parameters described previously.[9,10,22] In Figures 1 and 2 the results of such molecular orbital calculations on M_{19} and M_{38} clusters with fcc packing arrangements are illustrated. Although the clusters have O_h symmetries, the spherical pseudosymmetry is clearly discernible and the degeneracies of the jellium 1s, 1p, 1d,
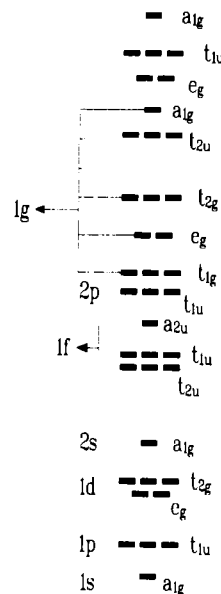
Figure 2. MO energy level diagram for an M_{38} metal cluster based on an fcc arrangement with O_h point group (s model used in the calculation).

2s, 1f, and 2p shells are only slightly lifted. The absence of a 1f shell in the former case arises because this structure does not have a sufficient number of atoms in one shell to create the required number of nodal planes.

The extended Hückel calculations indicate a degree of flexibility not obvious in the jellium model. For example, the M_{19} cluster could have a closed-shell configuration for M_{19}^+ and M_{19}^- depending on whether the 2s (a_{1g}) orbital is occupied. Similarly, M_{38} could be associated with $(M_{38})^{4+}$, $(M_{38})^{2-}$, or $(M_{38})^{8-}$, all of which would have significant HOMO-LUMO gaps. Although, the large negative charge associated with the last make it an unrealistic structure.

The jellium model approach does not, however, provide a satisfactory account of the closed-shell requirement for clusters that have been derived from the vertex sharing of icosahedra. In Table III the closed-shell requirements of these clusters within the jellium model are given. They do not correspond to the electron counts observed in such clusters[14-16] by Teo. The reasons underlying why these clusters do not conform to the jellium model are discussed in more detail below.

Clusters Based on Vertex-Shared Icosahedra. Two large Au-Ag clusters, $[Au_{13}Ag_{12}Br_8(PR_3)_{10}]^+$[14b] and $Au_{18}Ag_{20}Cl_{14}(PR_3)_{12},$[15] have been characterized by single-crystal X-ray crystallographic determinations and described in terms of two and three icosahedra sharing one and three vertices, respectively. An EHMO calculation using Au s orbitals only for a naked 25-atom cluster (i.e. without halide or phosphine ligands) has been completed as part of this research in order to illustrate the orbital interactions in a cluster with two icosahedra sharing a vertex. The interaction between two monocapped pentagonal antiprisms (i.e. nido-icosahedral fragments) of gold atoms is shown in Figure 3. The

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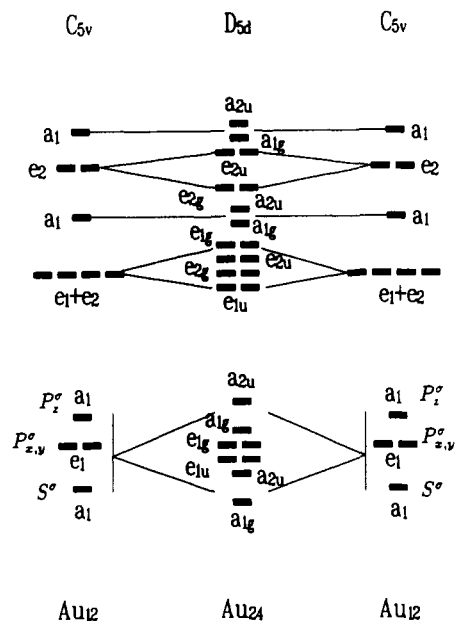(22) Wales, D. J.; Mingos, D. M. P. *Inorg. Chem.* **1989**, *28*, 2748.

Figure 3. Orbital interaction between two capped pentagonal antiprisms.
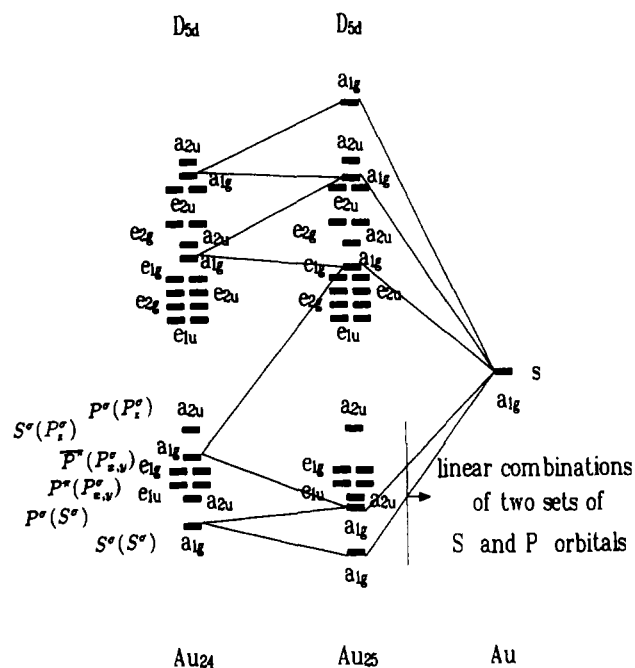

Figure 4. Orbital interaction in a vertex-shared bicosahedron.

molecular orbitals of each capped pentagonal antiprism are shown on each side of the figure. The bonding orbitals are $a_1(S^\sigma)$, $e_1(P^\sigma_{x,y})$, and $a_1(P^\sigma_z)$ in the point group C_{5v}. The antiprismatic combination of these two fragments results in a D_{5d} point group, and the bonding orbitals are $a_{1g}(S^\sigma(S^\sigma))$ and $a_{2u}(P^\sigma(S^\sigma))$ as a linear combination of the two S^σ orbitals from the two fragments. The P^σ orbitals split into $e_{1u}(P^\pi(P^\sigma_{x,y}))$, $e_{1g}(P^\pi(P^\sigma_{x,y}))$, $a_{1g}(S^\sigma(P^\sigma_z))$, and $a_{2u}(P^\sigma(P^\sigma_z))$. From the extent of the splitting of the orbitals, it can be seen that the overlap between the fragments is only small. This is to be expected in view of the long distance between the centers of these clusters.

The interaction of this $Au_{24}{}^{8+}$ fragment with Au^+ to complete the vertex-shared biicosahedron is shown in Figure 4. The $a_{1g}(s)$ orbital interacts most strongly with the $a_{1g}(S^\sigma(P^\sigma_z))$ and $a_{1g}(S^\sigma(S^\sigma))$. This results in the lowering of the total energy, but no additional bonding molecular orbitals are formed.

The notation used above for the resulting supracluster orbitals is based on the tensor surface harmonic approach to the linear combination of a perturbed spherical arrangement of clustes, as opposed to atoms in the original derived model for clusters.[4] The
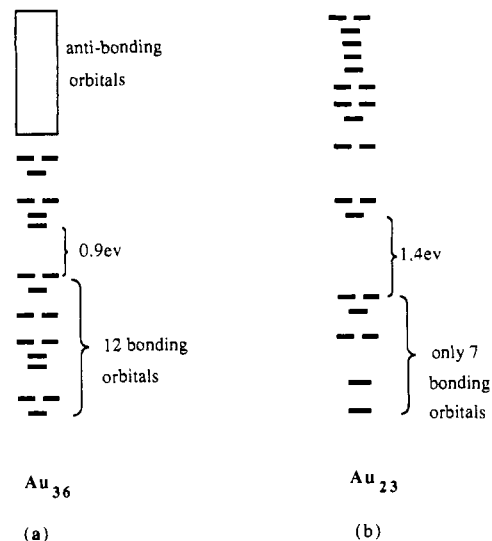

Figure 5. MO diagrams for a vertex-shared triicosahedron (a) and for a face shared biicosahedron (b).

fact that this is straightforward lies in the fact that the TSH model used for a cluster of atoms results in cluster orbitals with the same nodal characteristics as those of atomic orbitals. Therefore the aggregation of clusters can be described by the same methodology but with the use of S^σ, P^σ, and D^σ cluster orbitals instead of s, p, and d atomic orbitals.

The analysis above indicated that the bonding skeletal orbitals are simply the addition of the two sets of S^σ and P^σ bonding orbitals derived for each icosahedron. The interaction between these two sets of orbitals is small and leads to a spectrum of molecular orbitals that corresponds to a linear combination of the subsets.

Therefore, the closed-shell requirement for a pair of icosahedra sharing a vertex corresponds to the filling of $1S^\sigma$, $1P^\sigma$, $2S^\sigma$, and $2P^\sigma$, i.e. requires a total of 16 valence electrons. This contrasts with the closed-shell requirement of 20 valence electrons from a jellium model corresponding to $(1s)^2(1p)^6(1d)^{10}(2s)^2$ (see Table III). MO calculations (see Figure 5a) have also been completed for the cluster with three icosahedra sharing three vertices. There are 12 bonding orbitals that correspond to the linear combinations among the three sets of S^σ and P^σ bonding orbitals of a single icosahedron. It is apparent that clusters with two and three icosahedra sharing vertices have 2×8 (16) and 3×8 (24) s valence electrons. This contrasts with a jellium closed-shell structure of $(1s)^2(1p)^6(1d)^{10}(2s)^2(1f)^{14}$ given in Table III.

Therefore, it can be generalized that the total number of valence s electrons for gold clusters based on linked icosahedra is given by

$$n_s = 8n_p \qquad (1)$$

where n_s is the number of valence s electrons and n_p the number of polyhedra that form the supercluster. These closed-shell requirements are completely different from those derived above for clusters with close-packed arrangements and conforming to the jellium model.

Equation 1 is only valid for condensed clusters when the orbital interaction among those polyhedra forming the supracluster is small. The supraclusters that consist of vertex-sharing icosahedra provide such a class.

The additive nature of the electron count in these supraclusters is not too surprising in view of an icosahedral packing in the rare-gas clusters, Xe_n.[23] Since the orbital interaction between icosahedra is small when they are condensed through vertex sharing, the individual icosahedron unit with 8 valence electrons can be viewed as an inert-gas center. Each center satisfies the closed-shell requirement with an s^2p^6 configuration. Therefore, an icosahedral packing is preferred.
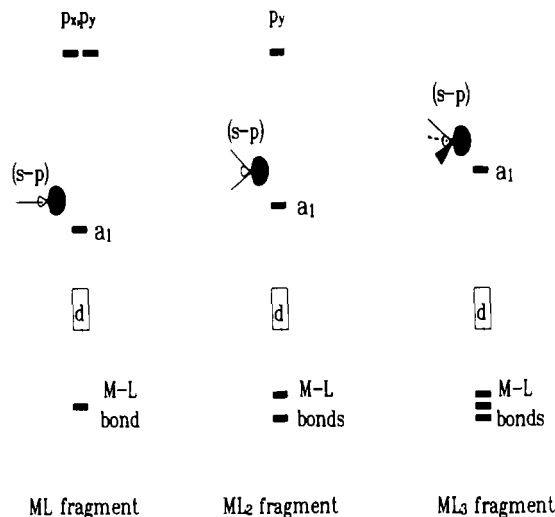
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Figure 6. Frontier orbitals of AuL_m ($m = 1-3$).

Clusters based on the vertex sharing of smaller polyhedra and face sharing of polyhedra (small or large) result in more close-packed structures. Such clusters conform to the structural jellium model because the overlaps between the adjacent polyhedra are larger. In such situations, not all of the linear combinations of orbitals are occupied and the closed-shell requirements are no longer additive. For example, calculations on clusters based on icosahedra sharing faces have demonstrated that some of the linear combinations are no longer bonding (see Figure 5b) and the additive relationships discussed above are no longer valid.

Effect of Ligands. It is important to emphasize that the closed-shell requirements of these linked icosahedral clusters are determined by the total number of metal s valence electrons associated with the cluster rather than the total number of valence electrons in the cluster. This is at variance with the usual polyhedral skeletal electron pair theory,[6] which is based on the total number of valence electrons in metal carbonyl clusters.

In the condensed clusters, gold atoms in the common units (vertices, edges, or faces) may not have ligands bonded to them and atoms in the noncommon units may have more than one ligand. The radial (s-z) hybridized orbital of each AuL_m ($m = 1-3$) fragment is still available for skeletal bonding no matter how many ligands (L) are associated to each gold atom. This can be understood in terms of the frontier orbitals of AuL_m ($m = 1-3$) fragments, which are shown in Figure 6. The addition of ligands involves interactions between the p orbitals of gold and the ligand orbitals although the Au p orbitals are not available for the skeletal bonding in the gold clusters. This leads to a complicated situation when the ligand electron pairs are included in the electron counting. Therefore an electron-counting scheme that involves only the gold valence electrons simplifies the problem, since each AuL_m fragment provides a radial frontier orbital for the skeletal bonding. The simplified s model developed above is applicable to both ligated and bare Au-Ag clusters.

Results. On the basis of a simplified molecular orbital analysis, the closed-shell requirements of two classes of high-nuclearity group 11 clusters have been defined. The closed-shell requirements of these clusters are determined primarily by the overlap of metal ns ($n = 5$, Ag; $n = 6$, Au) orbitals, although the $(n - 1)d$ orbitals also make a contribution to metal-metal bonding and np orbitals are important for accepting electron pairs from ligand lone-pair orbitals. In clusters with close-packed arrangements of metal atoms, the closed-shell electron requirements can be derived from a jellium type analysis corresponding to the filling of the following subshells: $1s < 1p < 1d < 2s < 1f < 2p < 1g < 2d < 3s < 1h$. Closed shells are achieved when the total number of valence electrons is 2, 8, 18, 20, 34, 40, 58, 68, etc. In contrast, group 11 clusters with structures based on the vertex sharing of ica-

sohedra have closed-shell electronic structures which represent multiplies of those of the individual icosahedra in the structure. A singly centered icosahedral cluster, e.g. $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$, is characterized by S^σ and P^σ bonding skeletal MO's, and a stable closed-shell configuration results when these are fully occupied, i.e. for 8 s metal valence electrons. When these icosahedra are vertex-linked, the skeletal molecular orbitals do not overlap sufficiently strongly to destroy this pattern and a set of n_p vertex-linked icosahedra are characterised by n_p S^σ and n_p P^σ skeletal MO's that require $8n_p$ s valence electrons in total.

Discussion. Gold, silver, and copper M^+ clusters that are formed in molecular beam experiments[20] have magic numbers at 3, 9, 21, 35, 41, 59, 93, and 199, which closely follow the predictions associated with a jellium type analysis. The high-symmetry fcc structures summarized in Table II with 9, 21, 35, and 93 represent good candidates for the structures of these magic numbers since they combine high symmetry, close packing, and jellium closed-shell structure simultaneously.

In the area of ligated clusters of group 11 metals, the icosahedron is the dominant structural moiety, which has been revealed in a number of single-crystal X-ray crystallographic determinations.[14-16] The higher nuclearity examples show a preference for vertex-linked icosahedra.

In the centered icosahedral gold cluster, $[Au_{13}Cl_2(PR_3)_{10}]$-$(PF_6)_3$,[17] the 8 gold valence electrons occupy the four skeletal orbitals (S^σ and P^σ). The $[Au_{13}Ag_{12}Br_8(PR_3)_{10}]^+$[14b] cluster compound synthesized by Teo can be described as two centered icosahedra sharing one vertex. Therefore, 16 metal valence electrons are expected for this cluster on the basis of the MO analysis presented above. The cluster $Au_{18}Ag_{20}Cl_{14}(PR_3)_{12}$[15] consists of three icosahedra sharing three vertices. It is characterized by 24 skeletal electrons derived from the metal s orbitals. More recently, Teo et al.[16] reported a 46-atom Au-Ag cluster, $Au_{22}Ag_{24}(PR_3)_{12}Cl_{10}$, which is composed of four 13-atom (Au_7-Ag_6) gold-centered icosahedra sharing six gold atoms, i.e. a tetrahedral supracluster. From the molecular orbital analysis developed above, we predict that the molecule should have a charge of +4, i.e. have a formula $[Au_{22}Ag_{24}(PR_3)_{12}Cl_{10}]^{4+}$, which corresponds to 32 gold and silver s valence electrons, i.e. for four vertex-linked icosahedra. The closed-shell requirements for higher nuclearity group 11 clusters based on vertex-shared icosahedra are summarized in Table I.

Teo has provided an alternative interpretation of the closed-shell requirements of linked icosahedra using his topological electron-counting rules[18] and a condensation principle. The following typical stoichiometries were proposed for these clusters: $L_{12}M_{36}(\mu\text{-}X)_{12}$, $L_{12}M_{46}(\mu\text{-}X)_{14}$, $L_{12}M_{56}(\mu\text{-}X)_{16}$, and $L_{12}M_{75}(\mu\text{-}X)_{20}$ (L = phosphine, X = halide), which are consistent with the MO analysis presented above. The presence of 12 phosphine ligands in these formulas is a result of steric considerations. The polyhedra listed in Table 1 generally have 12 atoms of the outer sphere that are suficiently exposed to coordinate phosphine ligands.

Some interest has been shown recently in the high-nuclearity gold clusters originally synthesized by Schmid[24] and formulated as $[Au_{55}Cl_6(PPh_3)_{12}]$, with a close-packed cuboctahedral structure. Fackler[19] has reformulated this cluster as $[Au_{67}Cl_8(PPh_3)_{14}]$ with six vertex-shared icosahedra, making an edge-shared tetrahedral supracluster. The closed-shell requirements defined in this paper may prove useful for providing circumstantial evidence for distinguishing these alternatively packed structures, when the experimental evidence regarding the stoichiometries becomes more generally accepted.

(24) Schmid, G. *Struct. Bonding* **1985**, *62*, 51.