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New Approach to Bonding in Transition-Metal Clusters and Related Compounds

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A cluster of atoms is treated as a perturbed spherical shell or an assembly of concentric spherical shells. This leads to an approximate classification of the cluster orbitals in terms of angular momentum quantum numbers l and m and (for orbitals constructed from atomic π and δ orbitals) the parity. The energies of the cluster orbitals are obtained approximately as functions of the quantum numbers and of the average angle ω between neighboring sites on the sphere, in a way which is independent of the fine details of the structure. The cluster orbitals formed from atomic σ orbitals increase in energy with l, but those formed from atomic π and δ orbitals are, by and large, bonding or antibonding depending on their parity. The method yields a general proof of the usual electron-counting rules for boron hydrides and provides similar rules for transition-metal cluster compounds. It also explains the common preference for triangulated-polyhedral structures, as well as showing how departures from such structures can arise.

1. Introduction

The nature of the bonding in polyhedral clusters of atoms has been a topic of interest for more than 25 years and is still important. Accumulated experience has led to the formulation of electron-counting rules[1-3] which are based on the well-known rule that a stable bonding scheme for an n-atom polyhedral cluster requires $n + 1$ electron pairs involved in skeletal bonding. Although this rule is "well-known", its validity rested until recently only on a number of calculations which either dealt with specific systems[4,5] (one of these[5] being manifestly erroneous) or assumed a high (cubic or icosahedral) symmetry in the effective potential.[6] Moreover, there is an exception: tetrahedral structures with five skeletal bonding pairs do not occur. A tetrahedron of atoms may be "electron precise"—that is, it may have the same number of skeletal electron pairs as edges, namely, in this case 6 or $n + 2$, rather than $n + 1$ (the P_4 molecule is an example)—or it may use only four electron pairs, as in B_4Cl_4.

Another general rule which has been given no theoretical foundation rests on the empirical observation that polyhedral structures very frequently have triangular rather than square or pentagonal faces. Thus the triangular prism is generally less stable than the octahedron, and the cube is less stable than the square antiprism which in turn is less stable than the "triangular dodecahedron" (the latter being a D_{2d} structure obtained by distorting an octahedron capped on two adjacent faces so that an edge is formed between the capping atoms[7]).

Recently, in an interesting series of papers, King and Rouvray[8] used a graph-theoretical approach to derive an explanation of the $n + 1$ rule. However, their method is based on the Hückel approximation in its simplest form and provides no explanation of the triangular-face rule, which it uses as a starting point. Moreover the graph theory provides information only on the distribution of eigenvalues and does not have anything to say about the form of the wave functions.

The theory described here provides a simple explanation both of the general $n + 1$ rule and of the exceptional tetrahedral case. At the same time it provides a vivid pictorial approach to the bonding and explains the triangular-face rule. No assumptions are made about the symmetry or structure of the cluster; indeed the key assumption ignores the structure altogether and requires merely that the molecule can be treated, as far as the valence electrons are concerned, as a perturbed spherical shell. That this is not as gross an approximation as might appear may be judged from the fact the conclusions apply quite as successfully to diatomic "clusters" as, for example, to icosahedral ones where the assumption of spherical symmetry might seem a better approximation.

The method can be applied not only to the bare clusters themselves but also to compounds like the binary carbonyls, where a cluster of metal atoms is surrounded by a cluster of carbonyl ligands. We shall in fact be able to see why it is that the same electron-counting rules can be applied, if suitably interpreted, to the electron-rich transition-metal compounds as well as to the electron-deficient boron hydrides. Mingos[9] has offered an explanation of this in the light of a calculation on an octahedral cluster; the present work supports his view, but in a more general and visualizable fashion.

The procedure we shall adopt is as follows.

(i) We begin by considering a spherical system, for which the angular part of the wavefunction is separable from the radial part. The angular part is a solution of

$$\nabla^2\psi = -l(l+1)\psi \qquad (1.1)$$

where

$$\nabla^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \qquad (1.2)$$

The scalar solutions of eq 1.1 are the familiar spherical harmonics (or *surface harmonics*) Y_{lm}, labeled by integer quantum numbers l (≥ 0) and m ($-l \leq m \leq l$). However we shall also use solutions of eq 1.1 in which ψ is a *vector* or *tensor* function of position; these are the vector and tensor surface harmonics.

(ii) The cluster is then treated as an assembly of atoms with nuclei arranged on the surface of a sphere. We obtain wavefunctions for this system by treating the magnitude of the spherical harmonic function at an atom site as the coefficient in an LCAO molecular orbital. This takes into account the actual structure of the cluster in a perfectly general way, except of course that variations in radial position are ignored. The procedure is not altogether novel; it can be used for example to derive the LCAO wavefunctions of a cyclic hydrocarbon C_nH_n from the wavefunctions of a particle on a circular ring or the wavefunctions of a linear polyene from those of a particle in a box. In both cases the results are precisely correct, though

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in the latter case it is necessary to be careful about the treatment of the ends. It has also been used by Eberhardt, Crawford, and Lipscomb[10] in a discussion of the bonding in $B_{12}H_{12}$, though rather inconclusively, and in a general qualitative and pictorial survey of molecular orbital theory by Hoffman, Ruedenberg, and Verkade.[11] The present procedure is novel, however, in that the orbital energies are obtained in a quantitative, though approximate, way and in that the π and δ orbitals are treated by reference to vector and tensor surface harmonics, respectively. The importance of this cannot be overemphasized; attempts to classify orbitals by reference to ordinary spherical harmonics—in effect, by counting nodes—do not distinguish between the nodes that are intrinsic to the atomic orbitals concerned and the nodes between atoms which alone are associated with antibonding character. It was for this reason that Eberhardt, Crawford, and Lipscomb[10] were unable to reach a clear conclusion about the electronic structure of $B_{12}H_{12}$.

(iii) We next assume that, notwithstanding the lowering of symmetry implied in stage ii, the orbitals so constructed retain approximately the symmetry characteristics of the spherical harmonics from which they were derived: namely, that there is no mixing between orbitals which differ in l or m and that a set of orbitals with a given l share the same energy. The latter assumption makes it possible to use the properties of spherical harmonics to derive a simple expression for the energy; the former implies that, after allowing for mixing between orbitals with the same l and m, the orbitals derived from the spherical harmonics are in fact the correct molecular orbitals for the system.

(iv) In this way we arrive at a classification of the cluster orbitals and their energies in terms of their l quantum number. Because of the $(2l + 1)$-fold degeneracy, this simplifies matters greatly, and because the spherical harmonics are so familiar, the nature of these sets of orbitals is very readily visualized.

2. Radial (σ) Orbitals

We begin with the *radial* or σ orbitals, namely, those that are constructed from atomic orbitals directed inward (or outward) from a cluster atom toward (or away from) the center of the cluster. We shall initially have in mind the polyhedral boranes, where the σ atomic orbitals are mostly s in character.

Now we know that if the cluster were indeed a sphere, the angular form of the molecular wave function would be a solution of eq 1.1—a spherical harmonic $Y_{lm}(\theta,\phi)$. We transfer this wavefunction to our actual cluster, which has atoms distributed over a sphere at angular positions (θ_i,ϕ_i), with $i = 1, 2, ..., n$, and at approximately equal distances r_i from the center. The spherical harmonic function values $Y_{lm}(\theta_i,\phi_i)$ are now interpreted as the coefficients c_i in an LCAO molecular orbital $\psi_{lm}{}^{\sigma} = \sum_i c_i \sigma_i$ formed from the σ atomic orbitals σ_i. For an octahedral cluster we obtain the molecular orbitals illustrated in Figure 1. There is one orbital with $l = 0$, which we may label as S and a set of three with $l = 1$ which we label as P. For the purpose of illustration, we use the real forms of the spherical harmonics, defined for $m > 0$ by[12a] eq 2.1.

$$Y_{lm}{}^{c} = 2^{-1/2}[(-)^m Y_{lm} + Y_{l,-m}] = 2^{1/2}\,\mathrm{Re}(Y_{l,-m})$$

$$Y_{lm}{}^{s} = -2^{-1/2}i[(-)^m Y_{lm} - Y_{l,-m}] = -2^{1/2}\,\mathrm{Im}(Y_{l,-m}) \qquad (2.1)$$

The S orbital is evidently strongly bonding, and the P orbitals are nonbonding (or weakly antibonding if we allow for the antibonding trans interaction). When we come to the D orbitals, with $l = 2$, we find only two nonzero ones, because d_{xy}, d_{xz}, and d_{yz} are all zero at the positions of the atoms. The two nonzero orbitals are both strongly antibonding, so we see that the energy increases with l, as the node count would lead us to expect. There can be only six independent orbitals, so this completes the list. If we were to continue with $l = 3, 4$, etc., any nonzero orbitals that we might find would be expressible as linear combinations of these six.

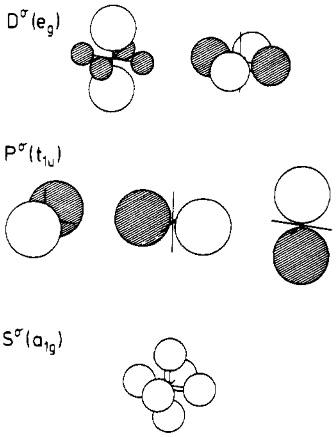

Figure 1. σ orbitals for an octahedral cluster.

These orbitals will be familiar as the symmetry orbitals for an octahedral set of six σ ligands, and indeed they were derived long ago for the B_6 octahedron by Longuet-Higgins and Roberts.[4] Here the high symmetry of the octahedron ensures that the spherical harmonic method yields precisely the correct orbitals for the system (remember that we are ignoring the interaction with the surface orbitals for the time being). However we anticipate that, even in clusters of low symmetry, the method will yield a set of n orbitals which will be mixed only slightly with each other by the low-symmetry part of the Hamiltonian. The major low-symmetry effect—the concentration of the atomic core potential at the atom sites—has already been incorporated by the transition from the basic spherical harmonic function to the LCAO wavefunction.

The energy $W_{lm}{}^{\sigma}$ of one of these orbitals is given by the usual quantum-mechanical formula as eq 2.2 where $\hat{F}$ is the

$$W_{lm}{}^{\sigma} = \int \psi_{lm}{}^{\sigma *}\hat{F}\psi_{lm}{}^{\sigma}\,d\tau \Big/ \int \psi_{lm}{}^{\sigma *}\psi_{lm}{}^{\sigma}\,d\tau \qquad (2.2)$$

Fock operator (effective one-electron Hamiltonian) for the system. According to our assumptions, W_{lm} will not depend much on m, so we seek an average value W_l which will serve for all $2l + 1$ orbitals in the set. This cannot be a simple average of the form $\sum_m W_{lm}{}^{\sigma}/(2l + 1)$, however, because some of the $\psi_{lm}{}^{\sigma}$ may vanish, as we have seen, and the corresponding $W_{lm}{}^{\sigma}$ is then undefined. Partly for this reason, but also because the ensuing algebra takes a particularly simple form, we take a weighted mean (eq 2.3).

$$W_l{}^{\sigma} = \Big[\sum_m W_{lm}{}^{\sigma}\int \psi_{lm}{}^{\sigma *}\psi_{lm}{}^{\sigma}\,dt\Big] \Big/ \Big[\sum_m \int \psi_{lm}{}^{\sigma *}\psi_{lm}\,dt\Big] = \Big[\sum_m \int \psi_{lm}{}^{\sigma *}\hat{F}\psi_{lm}{}^{\sigma}\,dt\Big] \Big/ \Big[\sum_m \int \psi_{lm}{}^{\sigma *}\psi_{lm}{}^{\sigma}\Big] \qquad (2.3)$$

Now the numerator of this expression is

$$\sum_m \sum_{ij} c_i{}^{*}c_j \int \sigma_i{}^{*}\hat{F}\sigma_j\,dt = \sum_{ij}\{\sum_m Y_{lm}(\theta_i,\phi_i)^{*}\,Y_{lm}(\theta_j,\phi_j)\}F_{ij}{}^{\sigma} \qquad (2.4)$$

where

$$F_{ij}{}^{\sigma} = \int \sigma_i{}^{*}\hat{F}\sigma_j\,dt \qquad (2.5)$$

and a standard theorem (the *spherical harmonic addition*

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[10] Eberhardt, W. H.; Crawford, B.; Lipscomb, W. N. *J. Chem. Phys.* **1954**, *22*, 989.

[11] Hoffman, D. K.; Ruedenberg, K.; Verkade, J. G. *Struct. Bonding (Berlin)* **1977**, *33*, 57.

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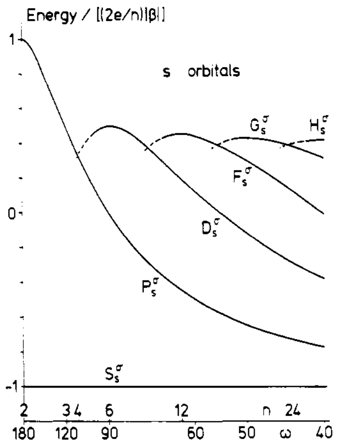

Figure 2. Energies of σ orbitals in arbitrary units.

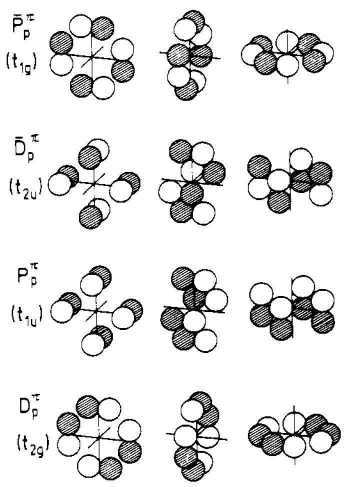

Figure 3. π-symmetry orbitals for an octahedral cluster.

theorem[12b,13] tells us that the quantity in braces depends only on the angular separation ω_{ij} between the two sites i and j. In fact

$$\sum_m Y_{lm}(\theta_i,\varphi_i)^* Y_{lm}(\theta_j,\varphi_j) = [(2l+1)/4\pi]P_l(\cos\omega_{ij}) \tag{2.6}$$

where $P_l(x)$ is the Legendre polynomial of degree l in x. Thus eq 2.4 becomes

$$[(2l+1)/4\pi]\sum_{ij} F^\sigma(\omega_{ij})P_l(\cos\omega_{ij}) \tag{2.7}$$

where we have made explicit the fact that the matrix element F_{ij}^σ depends, in view of our assumptions, only on the angular separation of the sites.

In the denominator of eq 2.3 we have exactly the same result, except that the matrix elements F_{ij}^σ are replaced by overlap integrals

$$\int \psi_{lm}^{\sigma *}\psi_{lm}^\sigma \, \mathrm{d}t = [(2l+1)/4\pi]\sum_{ij} S^\sigma(\omega_{ij})P_l(\cos\omega_{ij}) \tag{2.8}$$

and the average energy becomes

$$W_l^\sigma = [\sum_{ij} F^\sigma(\omega_{ij})P_l(\cos\omega_{ij})]/[\sum_{ij} S^\sigma(\omega_{ij})P_l(\cos\omega_{ij})] \tag{2.9}$$

This is already quite a simple expression, but it becomes more illuminating if we make the Hückel approximations:

$$\begin{array}{lll} S_{ij} \approx 0 & & i \neq j \\ F_{ij} \approx & \alpha^\sigma & i = j \\ & \beta^\sigma & i, j \text{ neighbors} \\ & 0 & \text{otherwise} \end{array}$$

and assuming also that all neighboring pairs have approximately the same angular separation ω, we find that

$$W_l^\sigma \approx [n\alpha^\sigma + 2e\beta^\sigma P_l(\cos\omega)]/n = \alpha^\sigma + (2e/n)\beta^\sigma P_l(\cos\omega) \tag{2.10}$$

where e is the number of neighboring pairs—that is, the number of *edges* in the polyhedron of atoms. The quantity $-P_l(\cos\omega)$ is plotted, for l = 0–5, in Figure 2 for values of ω from 180°, corresponding to $n = 2$, down to about 40°, corresponding roughly to $n = 32$. A nonlinear scale (abscissa proportional to $1/\omega$) is used so that points between $\omega = 70°$ and $\omega = 40°$, where n increases rapidly, are well separated. Note that the quantities plotted are functions of ω and that values of n are shown only as a guide. W_2^σ does not enter the picture until $n = 5$, because S^σ and P^σ orbitals suffice for $n \leq 4$, and in this region W_2^σ is meaningless because the ψ_{2m}^σ are linear combinations of ψ_{00}^σ and the ψ_{1m}^σ. Similarly W_3^σ is not shown for $n \leq 9$ and so on.

It is evident that the energy increases monotonically with l, as would be expected on intuitive grounds. We defer further discussion until the π orbitals have been dealt with but note particularly before we move on the factor $(2e/n)$ which appears in eq 2.10.

3. Surface (π) Functions

By π orbitals we mean, in accordance with the usual convention, those atomic orbitals which have exactly one node containing the radius vector from the center of the cluster to the atom in question. To see that an approach based on ordinary spherical harmonics, or in effect on counting nodes, is likely to fail, consider the π-symmetry orbitals for the octahedral cluster, depicted in Figure 3. Ignore for the moment the designations P^π, D^π, etc. and observe that the t_{2g} orbitals, which have two nodal planes, are likely to be more strongly bonding than the t_{1u}, which have only one, and are certainly not to be compared in energy with the D^σ orbitals (Figure 1), which also have two nodes. The difficulty is evidently due mainly to the fact that the nodes in this case are intrinsic to the p orbitals themselves, so that their presence does not confer any antibonding character. However, if these nodes are disregarded, we are left with no nodes by which the relative energies may be estimated. Furthermore, although there are no nodes of an antibonding nature, these orbitals are clearly not to be classified as S type.

The solution to this problem lies in the observation that a set of p orbitals on any one atom behaves like a set of unit vectors. If therefore we can find a *vector* function of θ and ϕ which satisfies eq 1.1, we can interpret its direction and magnitude at any site on the sphere as the direction and magnitude of a p orbital contribution to a wavefunction. Such functions are known; they are called vector surface harmonics and have been used in cosmology[14] and in the study of stellar pulsations,[15] as well as in the description of light propagation and scattering from a point source.[16] Their properties have been summarized, rather tersely, by Sandberg.[17] The mathematical details of the application of these functions to the present problem will be given elsewhere;[18] we note here only that from each spherical harmonic Y_{lm} we can construct *two* vector surface harmonics: one (called here "even") which

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(14) Lifshitz, E. M.; Khalatnikov, I. M. *Adv. Phys.* **1963**, *12*, 185.

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(16) Tough, R. J. A.; Stone, A. J. *Mol. Phys.* **1979**, *37*, 1469.

(17) Sandberg, V. D. *J. Math. Phys.* (*NY*) **1978**, *19*, 2441.

(18) Stone, A. J. *Mol. Phys.*, in press.

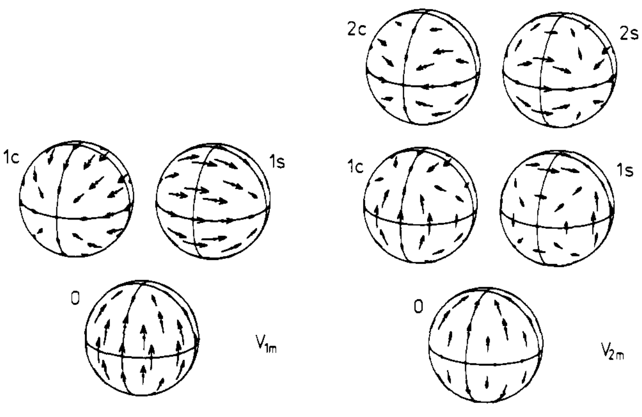

Figure 4. Even vector surface harmonics for $l = 1$ and 2. *mc* and *ms* label the real and imaginary parts of $\mathbf{V}_{lm}$ for $m \neq 0$, defined by analogy with eq 2.1.

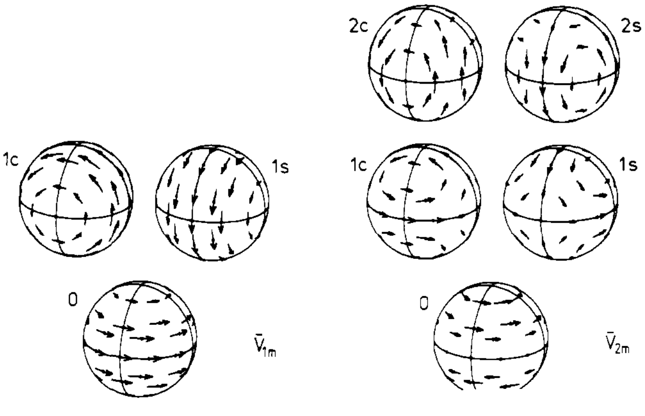

Figure 5. Odd vector surface harmonics for $l = 1$ and 2; notation as for Figure 4.

has the same behavior under the operation $\hat{P}$ of inversion as the parent Y_{lm}

$$\mathbf{V}_{lm} = \nabla Y_{lm} \qquad (3.1)$$

with

$$\hat{P}\mathbf{V}_{lm} = (-1)^l\mathbf{V}_{lm}$$

and one which has the opposite parity ("odd")

$$\bar{\mathbf{V}}_{lm} = \mathbf{r} \wedge \nabla Y_{lm} \qquad (3.2)$$

with

$$\hat{P}\bar{\mathbf{V}}_{lm} = (-1)^{l+1}\mathbf{V}_{lm}$$

These even and odd vector functions are illustrated in Figures 4 and 5. For purposes of illustration we use the real forms of the functions, defined by analogy with eq 2.1, and for each component the magnitude and direction of the function are shown at a number of points on the unit sphere by the length and direction of an arrow centered on each point. Note that there is no $\mathbf{V}_{00}$ or $\bar{\mathbf{V}}_{00}$, because Y_{00} is a constant function.

Now we may construct wavefunctions, as envisaged above, from each kind of vector surface harmonic. We shall obtain $2n$ independent functions, n of them from the "even" sequence and n from the "odd". The energies of these functions can be evaluated in much the same way as was described above for the σ functions; the details are given elsewhere.[18] In the Hückel approximation the energies W_l^π of the even functions and $\bar{W}^\pi$ of the odd functions take the form (3.3), where $w_l^\pi(\omega)$

$$W_l^\pi = \alpha^\pi + (2e/n)w_l^\pi(\omega)$$

$$\bar{W}_l^\pi = \alpha^\pi + (2e/n)\bar{w}_l^\pi(\omega) \qquad (3.3)$$

and $\bar{w}_l^\pi(\omega)$ are certain functions given in ref 18. Note once again the factor $(2e/n)$. In the numerical evaluation of the quantities w_l^π and $\bar{w}_l^\pi$, two β^π values are required, namely, β_σ^π to describe σ overlap of the π orbitals on adjacent sites and β_π^π to describe π overlap. The ratio of these two values is the only effective parameter, and its value does not affect the general pattern of the energy levels very much. In Figure 6 are illustrated the energies calculated by using parameters derived from a minimal basis set (STO-6G) SCF calculation on B_6H_6. The energies of the even functions are labeled P^π, D^π, F^π, etc., corresponding to $l = 1, 2, 3$, etc., and those of the odd functions are labeled $\bar{P}^\pi$, $\bar{D}^\pi$, $\bar{F}^\pi$, etc. We see that the former are bonding and the latter antibonding; this is in agreement with the graph-theoretical conclusion[8] that n of the π cluster orbitals are bonding and n antibonding but is much more explicit.

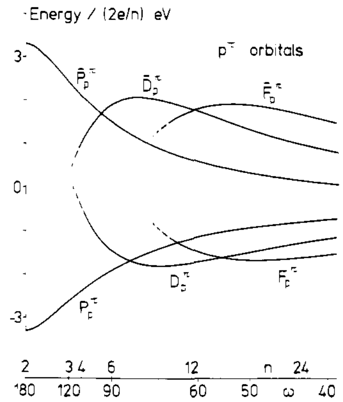

Figure 6. Orbital energies for π orbitals, calculated by using the Hückel approximation with parameters derived from a minimal basis set (STO-6G) SCF calculation on $B_6H_6^{2-}$.

4. Bonding in Boron Hydrides

We may now study Figures 2 and 6 in the expectation that the energies shown will be a good guide to the bonding in real clusters where d orbitals are not important—for example, in the boron hydrides. The first general point to note is that the nature of the polyhedron describing the shape of the cluster enters the energy expressions in two ways only: first, in the multiplicative factor $(2e/n)$ which appears in eq 2.10 and 3.3, and second, in the value of ω. Because of the first of these, Figures 2 and 6 should be thought of as scaled vertically by $(2e/n)$. Therefore so long as no antibonding orbitals are filled (and possibly even if some are) the bonding energy will be maximized if e is maximized. Consideration of Euler's theorem for polyhedra[19]

$$n + f = e + 2$$

where f is the number of faces, shows that for a fixed number n of vertices, the number of edges is maximized when the number of faces is maximized. This in turn occurs when all the faces are triangular, so we have a very simple and general explanation of the triangular-face rule.

A similar effect occurs in metals, where the cohesive energy is found empirically to be proportional to the square root of the number of nearest neighbors of each atom,[20] which is just the quantity $(2e/n)$ in the present notation. The absence of the square root in the present analysis arises because we have ignored so far the effect of a change of structure on the value of ω. We return to this below.

Examining Figure 6 in detail, we may observe that the energies of the even surface functions *decrease* (become more bonding) as l increases, so long as the l values remain mean-

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(19) Lakatos, I. "Proofs and Refutations"; Cambridge University Press: London, 1976.

(20) Ducastelle, F.; Cyrot-Lackmann, F. *J. Phys. Chem. Solids* **1970**, *31*, 1295. Cyrot-Lackmann, F.; Ducastelle, F. *Phys. Rev. B* **1971**, *4*, 2406. Heine, V. *Solid State Phys.*, in press.

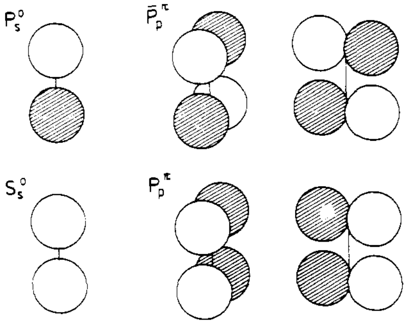

Figure 7. Orbitals for a diatomic cluster.

ingful. These orbitals are bonding for all n, though with some choices of β_σ^π and β_π^π the P^π energy, W_l^π, may become antibonding for large values of n. However we must, as Hoffmann and Lipscomb[4] noted, allow for mixing between the σ and π orbitals. The P^σ and P^π orbitals will repel each other in energy, and without the need for any quantitative calculations we can see that there will always be one bonding and one antibonding (or perhaps nonbonding) set of P orbitals. There is a similar interaction between the D^σ and D^π orbitals, and again one of the resulting energies will be bonding and one antibonding. We will run out of orbitals in the σ series just before we run out of π orbitals, because the σ orbitals start with an S^σ orbital whereas the π orbitals start with P^π. But the last orbital in the π sequence, the one with no σ partner, is already bonding in most cases, though examination of Figure 6 shows that this may not be true in the tetrahedral case, where $\omega = 109.5°$. Consequently the n π orbitals can all be thought of as correlating with bonding orbitals (although some of them may be largely or predominantly σ in character), while the n σ orbitals correlate with antibonding orbitals, with the single exception of the S^σ, which is always bonding.

The $\bar{W}_l^\pi$, on the other hand, are antibonding for any reasonable choice of β_σ^π and β_π^π. According to our hypothesis, there will be no interaction between the $\bar{P}^\pi$ and the P^σ or P^π because they differ in parity. If the actual structure lacks a center of symmetry, there may be a weak interaction which will merely make the $\bar{P}^\pi$ more antibonding and the P^π more bonding. In the same way, interactions between orbitals differing in l or m will occur, because the symmetry is not really spherical, but they are unlikely to affect the energy level pattern significantly.

The total number of bonding orbitals is therefore $n + 1$ exactly. Let us look at some particular cases in more detail.

Diatomic: $n = 2$, $\omega = 180°$. It is stretching credulity a little far to treat this as spherical. Nevertheless, a study of Figures 2 and 6 shows that there is an S^σ orbital and two P^π orbitals, all bonding, and a P^σ and two $\bar{P}^\pi$ orbitals, all antibonding. Filling the three $(n + 1)$ bonding orbitals gives the electronic structure of N_2, the most strongly bound diatomic, or of acetylene. To derive the P^π orbitals, we refer to Figure 4, where the three V_{lm} are illustrated. The two atoms of the cluster can be placed at any two diametrically opposed points, and we choose the "north pole" and the "south pole", so that the atoms lie on the z axis. In the $m = 0$ case, these are positions where the vector function V_{10} vanishes, so the corresponding cluster orbital vanishes also. From the functions V_{11}^c and V_{11}^s we obtain cluster orbitals by replacing the arrow at each atom position by a p orbital with its positive lobe directed toward the head of the arrow. This gives two nonzero p^π functions, which are illustrated in Figure 7. A similar procedure using the $\bar{V}_{lm}$ yields the $\bar{P}^\pi$ functions.

Triatomic: $n = 3$, $\omega = 120°$. Here there is an S^σ orbital (bonding), three P^π orbitals (bonding), and two P^σ and three $\bar{P}^\pi$ orbitals (antibonding) (Figure 8). Filling the $n + 1$ bonding orbitals gives the electronic structure of the cyclopropenyl cation. The degeneracy of the P^π and $\bar{P}^\pi$ orbitals is split by the low symmetry, but the qualitative picture is not affected.

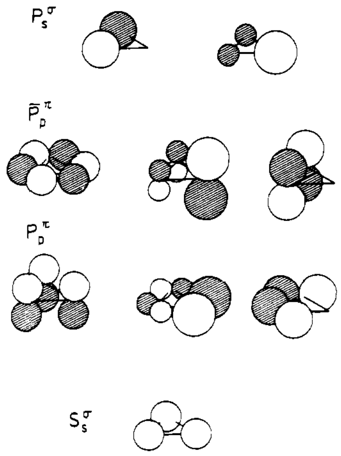

Figure 8. Orbitals for a triatomic cluster.

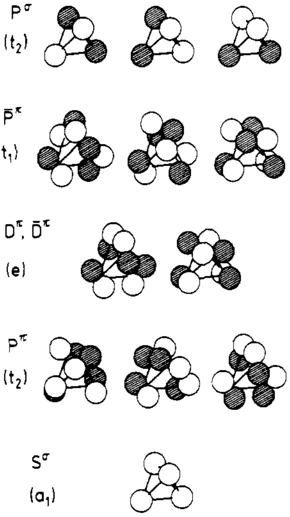

Figure 9. Orbitals for a tetrahedral cluster.

Tetraatomic: $n = 4$, $\omega = 109.5°$. Here we have an S^σ orbital (bonding) and three P^σ orbitals (antibonding) (see Figure 9). There are three P^π orbitals (bonding) and three $\bar{P}^\pi$ orbitals (antibonding). There is one D^π and one $\bar{D}^\pi$ orbital, which according to Figure 6 are approximately nonbonding. Consequently the four bonding orbitals may be filled, as in B_4Cl_4, or the nonbonding orbitals may also be filled, as in P_4.

This account may well seem rather glib, and indeed it does not explain why we should not fill only the D^π and not the $\bar{D}^\pi$ to give, apparently, a satisfactory 5-orbital bonding scheme. To see why this is not possible calls for a little special pleading but also throws some light on the extent to which the method can be trusted in general.

Standard group-theoretical methods show that the P^σ and P^π orbitals transform according to T_2 under the symmetry group T_d and that the $\bar{P}^\pi$ transform according to T_1. The D^π orbitals transform according to $E + T_2$ and the $\bar{D}^\pi$ according to $E + T_1$. Thus both the D^π and the $\bar{D}^\pi$ yield a pair of E functions, which are in fact identical and are the required orbitals, since the π orbitals transform as $E + T_1 + T_2$ overall. (The D^π and $\bar{D}^\pi$ orbitals need not be orthogonal in this case because of the lack of a center of symmetry.) The remaining D^π orbitals must be linear combinations of the orbitals already found, and because they are of T_2 symmetry, they can only be the P^π. The calculated D^π energy, which is a weighted average over all five orbitals, is therefore an average of the required E orbital energy and the T_2 or P^π and will be too low. Similarly the calculated $\bar{D}^\pi$ energy will be contaminated by the T_1 or $\bar{P}^\pi$ and will be too high. The required energy will be somewhere between these two limits and can be expected to be approximately nonbonding, as stated above. Also because the orbitals belong to the E representation, they are degenerate, and both or neither must be filled for a stable configuration.

It is apparent that the predictions of the theory must be treated with caution when only a few of a set of orbitals with a particular l are significant and the rest are not null. Fortunately the prospects are better in general than the tetrahedral case might lead us to suppose, for inspection of Figures 2 and 6 shows that new sets of orbitals are usually strongly bonding or antibonding when they enter the picture, so that errors in their energies are unlikely to modify the qualitative conclusions of the theory.

Octahedron: $n = 6$, $\omega = 90°$. We see here an S^σ orbital (bonding), three P^σ orbitals (nonbonding), and two D^σ orbitals (antibonding) as previously shown in Figure 1. Also there are three P^π and three D^π orbitals, all bonding, the P^π made more so by interaction with the P^σ which become antibonding as a result. Finally the $\bar{P}^\pi$ and the $\bar{D}^\pi$ are antibonding and do not mix with any of the other orbitals (Figure 3). Thus there are in total seven bonding orbitals, as established by Longuet-Higgins and Roberts.[4]

Icosahedron: $n = 12$, $\omega = 63.4°$. Here we have one S^σ and three P^σ (bonding) and five D^σ and three F^σ (antibonding). There are three P^π, five D^π, and four F^π orbitals, all bonding, but the interaction between P^σ and P^π yields one bonding set and one nonbonding or antibonding set, so that there are 13 bonding orbitals in all, as Longuet-Higgins and Roberts showed.[4] The three $\bar{P}^\pi$, five $\bar{D}^\pi$, and four $\bar{F}^\pi$ orbitals are all antibonding. It will be observed that the result is obtained quite unambiguously, whereas the attempt[10] to determine orbital energies from nodal structure alone (i.e., by relating the tangential orbitals to ordinary spherical harmonics rather than vector surface harmonics) was unable to discriminate between what we call here the F^σ and the F^π. Moreover we have no need to inspect the orbitals to determine their energies, though their form can be obtained readily if required with the help of Figures 4 and 5.

5. Relationship between Structures

Let us return now to an examination of the effect of a change of structure on the bonding. We consider for definiteness the relationship between the octahedron and the trigonal prism, but the conclusions are more general. Two things happen when the structure is changed from octahedral to trigonal prismatic: the value of $(2e/n)$ falls from 4 to 3, and the value of ω falls from 90 to 82° $(=2 \arctan (3^{1/2}/2))$ if all bond lengths remain equal. Now Figure 2 shows that this change in ω causes a marked drop in the energy of the P^σ orbitals, which are the lowest unoccupied orbitals in the $B_6{}^{2-}$ cluster, while there is little change in the S^σ energy or in the π orbital energies (Figure 6). For the $B_6{}^{2-}$ cluster, therefore, there is no advantage in adopting the trigonal-prism structure. If some of the P^σ orbitals were occupied, however, the considerable lowering of their energy could be expected to offset the loss of bonding energy caused by the adverse value of $(2e/n)$. This evidently happens in prismane, C_6H_6, which has 9 skeletal electron pairs. We can expect quite generally that the presence of more than $n + 1$ electron pairs will favor the adoption of a more open structure than the fully triangulated polyhedron.

6. Transition-Metal Clusters

The bonding in transition-metal clusters is more complicated, but for this very reason a systematic classification can be particularly valuable. There are several sources of complication.

(i) Whereas in the boron hydrides we could treat the σ orbitals as mostly s, we have in the transition-metal case three kinds of σ orbital, which for a first-row transition-metal atom at $\theta = \phi = 0$ are the 4s, $4p_z$, and $3d_z{}^2$ orbitals. From each kind of atomic orbital we can derive a set of n orbitals $\psi_{lm}{}^\sigma$, which we refer to below as the s^σ, p^σ, and d^σ sets. Their energies are evaluated by the same procedure as before, but we must remember that the symmetry axes of σ orbitals on adjacent atoms are inclined at an angle ω to each other. If the nuclearity of the cluster changes, the distance between atoms will not change, at least to a rough approximation, but the angle ω between neighbors will change, and this will modify the Fock matrix element (resonance integral) in the p^σ and d^σ cases. This does not however cause any fundamental difficulty; and in particular it does not affect the qualitative pattern of σ energy levels shown in Figure 2.

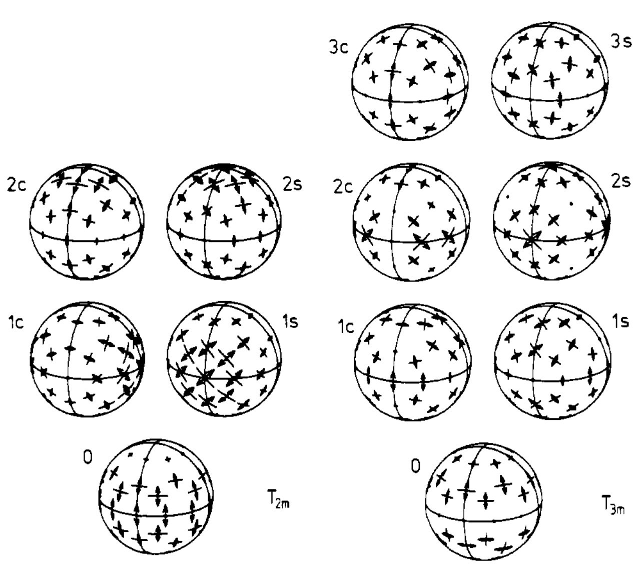

Figure 10. Even tensor surface harmonics for $l = 2$ and 3. mc and ms label the real and imaginary parts of T_{lm} for $m \neq 0$, defined by analogy with eq 2.1.

(ii) Similarly the π orbitals comprise, for an atom at (0,0), not only the $4p_x$ and $4p_y$ but also the $3d_{xz}$ and $3d_{yz}$. These pairs each give rise to an even and an odd set of $\psi_{lm}{}^\pi$, which we denote by p^π, $\bar{p}^\pi$ and d^π, $\bar{d}^\pi$ in what should be an obvious notation. Again the matrix elements depend in different ways on the angle between neighbors, but again the qualitative energy level pattern is not significantly different.

(iii) There are also δ orbitals to contend with. For an atom at (0,0) these are the $3d_{x^2-y^2}$ and the $3d_{xy}$. They are handled by using tensor surface harmonics; the details will be given elsewhere,[18] and we give here only a summary of the results, since it emerges that the δ orbitals are essentially nonbonding.

Tensor Surface Harmonics. In many ways these are analogous to the vector surface harmonics. Two tensor surface harmonics can be constructed from each Y_{lm}: an even one T_{lm}, with the same parity as the parent spherical harmonic, and an odd one $\bar{T}_{lm}$, with the opposite parity. The first allowed value of l is 2. These functions are illustrated for $l = 2$ and 3 in Figures 10 and 11, which show the real forms, defined by analogy with eq 2.1. The figures are most easily understood in terms of the wave-functions which are to be constructed from each harmonic; the arrows from each site represent the directions of the positive lobes of a d^δ orbital which would be the contribution to the wavefunction of an atom at that site, while the length of each arrow is proportional to the magnitude of the LCAO coefficient.

As in the case of the $\psi_{lm}{}^\pi$ and $\bar{\psi}_{lm}{}^\pi$, the $\psi_{lm}{}^\delta$ and $\bar{\psi}_{lm}{}^\delta$ turn out to be bonding and antibonding, respectively, and tend to become more bonding or antibonding with increasing l. Once again, the energies are proportional to $(2e/n)$ in the Hückel approximation. The strength of bonding or antibonding

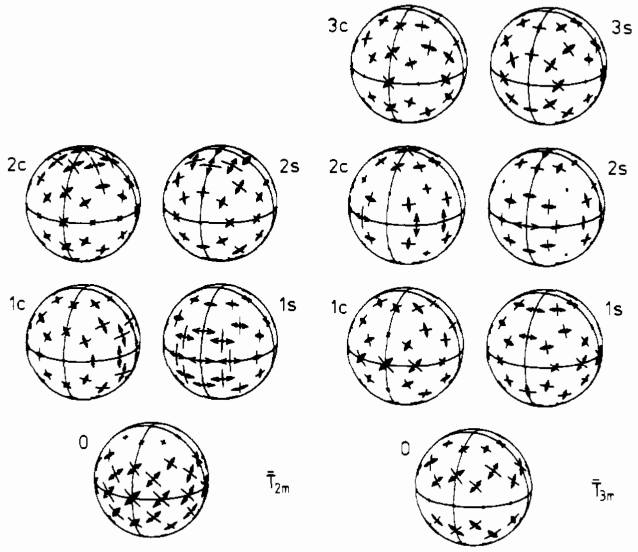

Figure 11. Odd tensor surface harmonics for l = 2 and 3; notation as for Figure 10.

Table I. Cluster Orbitals Formed from Atomic s, p, and d Orbitals[a]

atomic orbital	cluster orbital sequence	no. and type of cluster orbitals			
s	s^σ	1 S_s^σ	3 P_s^σ	5 D_s^σ	7 F_s^σ
p	p^σ	1 S_p^σ	3 P_p^σ	5 D_p^σ	7 F_p^σ
	$\underline{p}^\pi$		3 $\underline{P}_p^\pi$	5 $\underline{D}_p^\pi$	7 $\underline{F}_p^\pi$
	$\bar{p}^\pi$		3 $\bar{P}_p^\pi$	5 $\bar{D}_p^\pi$	7 $\bar{F}_p^\pi$
d	d^σ	1 S_d^σ	3 P_d^σ	5 D_d^σ	7 F_d^σ
	$\underline{d}^\pi$		3 $\underline{P}_d^\pi$	5 $\underline{D}_d^\pi$	7 $\underline{F}_d^\pi$
	$\bar{d}^\pi$		3 $\bar{P}_d^\pi$	5 $\bar{D}_d^\pi$	7 $\bar{F}_d^\pi$
	$\underline{d}^\delta$			5 $\underline{D}_d^\delta$	7 $\underline{F}_d^\delta$
	$\bar{d}^\delta$			5 $\bar{D}_d^\delta$	7 $\bar{F}_d^\delta$

[a] For a cluster of n atoms, the required orbitals are obtained by taking the first n nonzero orbitals in each row.

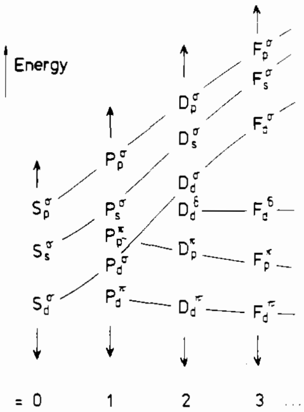

Figure 12. Scheme of even orbital energies for a transition-metal cluster.

character is however weaker, by a factor of 2 or 3, than for the corresponding d^π orbitals, and in any case the strength of interaction between d orbitals on neighboring atoms is weaker than for s and p orbitals. An SCF calculation on Fe_2 at an internuclear separation of 5 bohr radius (2.6 Å), using the minimal basis set recommended by Basch et al.[21] showed that the largest 3d–3d Fock matrix element was about −0.8 eV, whereas the 4s–4s Fock matrix element was about −2 eV. Thus we can expect the d^δ orbitals to have very little effect on the bonding and to be occupied in all transition-metal clusters.

7. Bonding in Transition-Metal Clusters

We are now in a position to survey the bonding in transition-metal clusters and their compounds. First, we note that the metal cluster can be expected to adopt a triangulated-polyhedral structure, because of the $(2e/n)$ factor in all the energy formulas. It is worth noting in this connection that the ligands also frequently adopt a triangulated-polyhedral structure, for reasons which are not understood, and it may be conjectured, notwithstanding the prevailing view to the contrary, that this is evidence of some interaction between occupied orbitals on one ligand (such as the CO σ or π) and vacant orbitals on its neighbors (such as the CO π^*), for this too would lead to a stabilization proportional to $(2e/n)$.

We adopt the approach on which is based the 18-electron rule for mononuclear complexes of group 8 transition metals: we suppose that all valence orbitals (3d, 4s, and 4p in the case of a first-row transition metal) will be occupied either by electrons from the metal itself or by electrons donated from the ligands; *except* that in the polynuclear case we shall find orbitals which are both high in energy and directed toward the center of the cluster, so that they are not available for bonding and remain vacant. For clusters with nuclearity greater than 4 it emerges that there are $2n - 1$ such orbitals, leaving $7n + 1$ available for cluster bonding. Moreover, as noted by Mingos[9] in the octahedral case, the $2n - 1$ inaccessible orbitals correspond directly to the $2n - 1$ vacant orbitals in a boron hydride with the same structure. In deriving this result it will be necessary to make certain assumptions as to the relative energies and the strength of interaction of the various sets of orbitals concerned, and these assumptions may not be universally valid. However the method, being essentially an approximate classification by symmetry, is not dependent on the details of such assumptions, and the arguments can easily be modified to take account of different circumstances.

With this caveat established, we proceed. We treat the ligands, like the metal atoms, in cluster terms, so that the σ donor orbitals form a sequence of S^σ, P^σ, etc. orbitals. We then anticipate that for any vacant and accessible metal orbital there will be a ligand σ orbital of the same symmetry to act as a donor orbital. This may be a false assumption for some ligand geometries, in which case the electron-counting rules will have to be modified, as happens in the mononuclear case for square-planar Ni, Pd, and Pt complexes. Apart from this, the detailed arrangement of the ligands is not considered, and indeed is largely irrelevant. The detailed structure is not, on this view, a reflection of major bonding effects. Any reasonably sane distribution of the ligands around the metal cluster will result in satisfactory bonding if the electron count is satisfactory, and the detailed structure is a matter of optimization among a range of broadly satisfactory structures. Johnson's view,[22] that the structure is determined primarily by packing considerations, is entirely consistent with this, for good packing of the ligands around the metal cluster ensures stronger bonding overlap. Again, the frequently observed fluxional behavior of such molecules, which can be explained very simply in terms of the metal cluster rotating within the ligand cluster,[22] fits very well with a model in which reasonably satisfactory bonding can be maintained at any relative orientation of the metal and ligand clusters.

The orbitals available can be classified in the way outlined above, as follows. We ignore initially the interaction between different sets of orbitals.

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(21) Basch, H.; Hornback, C. J.; Moskowitz, J. W. *J. Chem. Phys.* **1969**, *51*, 1311.

(22) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1976**, 211. Johnson, B. F. G.; Benfield, R. E. *J. Chem. Soc., Dalton Trans.*, **1980**, 1743.

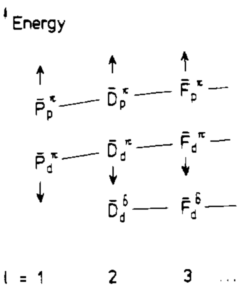

Figure 13. Scheme of odd orbital energies for a transition-metal cluster.

4s Orbitals. These form the s^σ sequence, comprising one S_s^σ, three P_s^σ, five D_s^σ, etc., from which we take the first *n* nonzero orbitals. These orbitals increase in energy from bonding to antibonding as we proceed along the series from $l = 0$. See Figure 12 and Table I.

4p Orbitals. These form the p^σ sequence, comprising S_p^σ, P_p^σ, D_p^σ, etc, the p^π sequence P_p^π, D_p^π, etc., and the $\bar{p}^\pi$ sequence $\bar{P}_p^\pi$, $\bar{D}_p^\pi$, etc. From each sequence we take the first *n* nonzero orbitals. The energies of the p^σ sequence are similar to those of the s^σ sequence, but somewhat higher; the p^π are bonding, by and large, with energy decreasing with increasing *l* (Figure 12), while the $\bar{p}^\pi$ are antibonding, with energy increasing with increasing *l* (Figure 13). The even and odd orbital energies are shown on separate diagrams to avoid confusion as far as possible; remember that according to our assumptions they do not mix.

3d Orbitals. These form a set of *n* d^σ orbitals, a set of *n* d^π orbitals (even), and a set of *n* $\bar{d}^\pi$ orbitals (odd), much as for the 4p orbitals but at lower energy, and a set of *n* even and *n* odd orbitals from the d^δ and $\bar{d}^\delta$ sequences, comprising D_d^δ, F_d^δ, etc. and $\bar{D}_d^\delta$, $\bar{F}_d^\delta$, etc., respectively.

Now let us consider qualitatively how the interaction between the sets of orbitals with the same symmetry will affect the energy level pattern. Consider first the odd orbitals (Figure 13). Interaction between the $\bar{P}_p^\pi$ and the $\bar{P}_d^\pi$ will push the former up in energy and the latter down. What can we say about the spatial distribution of the resulting molecular orbitals? The higher of the two sets is strongly antibonding (both $\bar{P}_p^\pi$ and $\bar{P}_d^\pi$ are antibonding to begin with), and it can only achieve that if the orbitals mix in such a way as to point inward toward the center of the cluster. Thus this set of orbitals is not only antibonding, but inaccessible to ligand electrons; it will remain empty. The lower of the two resultant sets of orbitals, on the other hand, is relatively weakly antibonding, which it can achieve only if the orbitals hybridize in such a way as to point outward, so minimizing the interaction between orbitals on neighboring atoms. These orbitals, therefore, are good acceptors for ligand electrons. In the same way, interaction between the $\bar{D}_p^\pi$ and the $\bar{D}_d^\pi$ will yield a strongly antibonding set of inward-pointing orbitals and a relatively weakly antibonding set of outward-pointing orbitals. The presence of the $\bar{D}_d^\delta$ will not modify this picture significantly, and we may expect them to be occupied and not greatly involved in ligand bonding. The same applies to the $\bar{F}$, $\bar{G}$, etc. orbitals if the nuclearity is high enough for them to enter the picture. In terms of orbital counting, then, we can regard the *n* $\bar{p}^\pi$ orbitals as correlating with *n* inaccessible antibonding orbitals, while the remaining odd molecular orbitals are filled either by metal electrons or by donation from ligands.

The diagram (Figure 12) for the even orbitals contains two kinds of orbital sequence. The s^σ, p^σ, and d^σ progress from strongly bonding when $l = 0$ to strongly antibonding for the largest relevant value of *l*. The p^π, d^π, and d^δ orbitals, on the other hand, are bonding for all relevant *l*. The S^σ orbitals will mix with each other, to yield one strongly bonding orbital (which will necessarily be composed of inward-pointing hybrids), one of intermediate energy, and one of higher energy. Even the highest of these can have no nodes between the atoms and so is at worst nonbonding, and it can only achieve that by being composed of outward-pointing hybrids. Consequently it is a good acceptor orbital if not actually bonding.

We may in fact generalize as follows. Orbitals which are strongly bonding within the cluster must be inward-hybridized to achieve the necessary bonding overlap; they will be inaccessible to the ligands but occupied by cluster electrons. Orbitals which are strongly antibonding will be inward-hybridized for the same reason; they will be inaccessible to electrons and will remain empty. Orbitals which are intermediate in energy will tend to be outward-hybridized; whatever their energy they will be accessible to ligands and so will be occupied either in their own right or as a result of donation from the ligands.

Turning now to the even P orbitals, we have a more complicated picture, with five sets of orbitals to consider. Moreover the picture is different for low and high nuclearity. For low nuclearity, the P^σ orbitals are antibonding, while the P^π are quite strongly bonding. We expect mixing of the P^σ to yield a strongly antibonding, inaccessible set and two less strongly antibonding, more accessible sets. For higher nuclearity ($n > 6$), the P^σ orbitals are bonding and the P^π weakly bonding or antibonding, so it is the latter which combine to yield an inaccessible set. The result in terms of electron counting is the same: one of the five sets of P orbitals is inaccessible. The appearance of the weakly bonding d^δ orbitals does not change the picture for the D, F, etc. orbitals. By the time the orbitals are all used up, however, we know that the most strongly antibonding orbital is one of the σ ones. Thus for the purposes of orbital counting we may consider that, for each value of *l except* $l = 0$, the p^σ set of orbitals is inaccessible to electrons. This gives $n - 1$ inaccessible orbitals, which with the *n* inaccessible odd orbitals makes $2n - 1$ inaccessible orbitals in all. Note that the inaccessible orbitals comprise (or more precisely, correspond in symmetry with) a $\bar{p}^\pi$ set and all but the S^σ member of a p^σ set and in this respect are precisely analogous to the vacant orbitals in a boron hydride. We see therefore in a quite general way what Mingos[9] pointed out for the octahedral case, that the same electron-counting rules work for the electron-rich transition-metal complexes as for the electron-deficient boron hydrides because of the similarity of the vacant orbitals in the two cases. Lauher[23] has also stressed the importance of the antibonding orbitals in the derivation of the electron count.

We can expect that the tetrahedral cluster will not obey this general rule, for the same kind of reason as before. A monoatomic "cluster" clearly does not, for none of its 9 orbitals is inaccessible to electrons, except in well-understood cases such as the square-planar platinum complexes. We had better treat the diatomic and triatomic clusters, as well as the tetraatomic, as special cases, though still within the general framework of the scheme.

Tetrahedral Clusters. The general argument applies quite nicely to the S, P, and D orbitals, yielding 6 inaccessible orbitals. There are no D^σ orbitals; the D_p^π and $\bar{D}_p^\pi$ must be taken together as an E pair, as before, and so must the D_d^π and the $\bar{D}_d^\pi$. The δ orbitals, like the π orbitals, transform as $T_1 + T_2 + E$ in T_d, and of these the T_1 and T_2 will mix with the corresponding P orbitals, but probably not to any great extent. In any case, mixing of d^δ orbitals with p^π or d^π cannot yield a hybrid which points inward or outward, so there will be no change in the number of inaccessible orbitals. There remain, then, three pairs of E orbitals. We saw previously that the E orbitals were more or less nonbonding in the tetrahedral

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[23] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305; **1979**, *101*, 2604.

case, and this implies that the three pairs of E orbitals in the present case will be nonbonding also and will interact weakly with each other. Consequently they will remain accessible, so that the only inaccessible orbitals are the six already found. This leaves 30 accessible orbitals for 60 electrons, as observed for example in $Rh_4(CO)_{12}$.

Triatomic Clusters. The general rule fails here for a different reason. Of the five "inaccessible" orbitals, three are symmetric with respect to the plane of the three atoms. They are like the P^σ orbitals and one component of the $\bar{P}^\pi$ shown in Figure 8, except that they are constructed from inward-pointing hybrids and they can be expected to be inaccessible to ligands. However the other two, the remaining components of the antibonding $\bar{P}^\pi$ set, are antisymmetric with respect to the plane of the cluster and are in fact accessible to ligands above and below. Consequently there are only three genuinely inaccessible orbitals in this case, so that 24 accessible orbitals remain to take 48 electrons, as in $Fe_3(CO)_{12}$. In localized-orbital terms, the three inaccessible orbitals are just the three metal–metal antibonding orbitals, as one would expect. Nevertheless the other two "inaccessible" orbitals are high in energy, and it is not surprising that there exist 44-electron complexes such as $Pt_3(CO)_6{}^{2-}$, where all the ligands lie in the plane of the Pt_3 cluster[24] and these orbitals remain empty.

Actually, in this planar case, one would expect only 42 electrons, because there is an A_2'' orbital constructed from Pt p orbitals which is nominally bonding (it is one of the $P_p{}^\pi$ set) but is high in energy and of the wrong symmetry to accept ligand electrons. In fact similar 42-electron complexes are known,[25] and Lauher[23] finds that the last electron pair in the 44-electron cluster is accommodated not in the metal cluster but in an A_2'' orbital on the ligands. Moreover this is composed largely of CO π^* orbitals, which supports the view expressed above that there can be significant bonding interaction between the ligands.

Diatomic Clusters. In the same way, the number of truly inaccessible orbitals in the diatomic is not 3 but 1, corresponding to the metal–metal antibonding P^σ orbital. There are 17 accessible orbitals for 34 electrons, as in $Fe_2(CO)_9$ and $Rh_2(CO)_8$.

8. Clusters with Interstitial Atoms

A number of clusters have interstitial atoms at the center, as for example in $HRu_6(CO)_{18}{}^-$ and $Ru_6(CO)_{17}C$. The hydride provides one orbital of S type, which can be expected to interact strongly with the inward-pointing S^σ orbital to yield a bonding and an antibonding combination. The new orbital therefore correlates with a new inaccessible orbital, and there is no change in the electron count. The same applies to the interstitial carbide, where the four new orbitals all become inaccessible, as pointed out by Lauher.[23] Similarly, in the Rh_{13} cluster in $Rh_{13}(CO)_{24}H_3{}^{2-}$, where one of the Rh atoms is interstitial,[26] the electron count is as for a 12-atom cluster, namely, $2(7n + 1) = 170$.

9. Conclusion

The results of this paper may be summarized as follows. By assuming that a cluster compound can be treated approximately as a set of concentric spherical shells, we have established a symmetry classification of the cluster orbitals. This classification uses the usual azimuthal and magnetic quantum numbers l and m, together with the parity, which for cluster orbitals derived from π or δ atomic orbitals may be either even or odd for each l. Interactions between orbitals differing in l, m, or parity are assumed to be negligible for the purposes of a qualitative description of the bonding. Using this classification for a transition-metal cluster carbonyl like $Co_6(CO)_{16}$, it is necessary to consider the interaction of at most six metal-cluster orbitals and two ligand-cluster orbitals at a time. This is an impressive simplification compared with the total number of 54 metal and 32 ligand orbitals, especially as the detailed structure of the complex does not have to be considered.

The energy of a cluster orbital is approximately independent of its quantum number m, and an approximate expression for the energy of a set of orbitals with a given l and parity is easy to calculate. It follows very straightforwardly that the number of skeletal electron pairs needed for bonding in a boron hydride with n boron atoms is $n + 1$. It is also easy to show that the bonding energy is maximized if the polyhedron of atoms has as many triangular faces as possible.

Another advantage of the method is that the form of the cluster orbitals is very easy to visualize, with the help of the illustrations given in this paper. This is particularly useful in dealing with transition-metal clusters, where the result in terms of electron counting is by no means so clear-cut as in the case of first-row atom clusters, largely because there are so many more orbitals to consider. The method identifies $2n - 1$ orbitals (except for the tetrahedron, where there are six) which are likely to be vacant, leaving $7n + 1$ available for cluster electrons. However some of the $2n - 1$ may be occupied in particular cases, modifying the electron count, and because the orbitals in question are so easily visualized, it is easy to see which are accessible to electrons in a given structure.

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