Table I

Summary of the CVMO's Derived from the Polyhedral Skeletal Electron Pair Approach[3,5]

polyhedral type	CVMO's[a,b]	relationship between F and V	examples
electron-precise or cubic polyhedra	$15V/2$ ($V \geqslant 4$)	$V = 2F - 4$	$Ir_4(CO)_{12}$, $Ni_8(PPh)_6(CO)_8$
closo deltahedra	$7V + 1$ ($V \geqslant 5$)	$F = 2V - 4$	$Os_5(CO)_{15}^{2-}$
nido deltahedra	$7V + 2$ ($V \geqslant 4$)	$F = V$ (pyramids)	$Os_5C(CO)_{15}$
arachno deltahedra	$7V + 2$ ($V \geqslant 4$)		$Fe_4H(CO)_{13}^-$–butterfly geometry

Condensed Polyhedra Derived from Components with V_1, $(CVMO)_1$, and V_2, $(CVMO)_2$, Vertices and Cluster Valence Molecular Orbitals[9]

vertex sharing:	edge sharing:	triangular face sharing:
$(CVMO)_1 + (CVMO)_2 - 9$	$(CVMO)_1 + (CVMO)_2 - 17$	$(CVMO)_1 + (CVMO)_2 - 24$

[a] V = number of vertices; F = number of faces; CVMO = number of bonding cluster valence molecular orbitals.[7] [b] The number of skeletal electron pairs (N) is related to CVMO by $N = CVMO - 6V$; e.g., for electron-precise polyhedra $N = 15V/2 - 6V = 3V/2$, for closo deltahedra $N = 7V + 1 - 6V = V + 1$, etc.

tron-precise polyhedra or cubic polyhedra and are characterized by $15V/2$ CVMO's. Since for these polyhedra $V = 2F - 4$, then

$$\begin{aligned} CVMO &= 15V/2 = 8V - V/2 \\ &= 8V - F + 2 \end{aligned}$$

I.e., X in eq 1 must equal 0.

Rule 2: Capping an N-gonal Face of a Polyhedron Leads to an Increase of X by $N - 3$. In the PSEPT, the capping principle has been widely used[6] and states that the CVMO increases by 6 on capping a face with a single atom. Since this process increases V by 1 and F by $N - 1$, it then follows that X must increase by $N - 3$.

Rule 3: $X = 0$ for All Pyramids. In the PSEPT, pyramids are examples of nido clusters[3] that are characterized (Table I) by $7V + 2$ CVMO's. Since for pyramids $F = V$, the following is true:

$$\begin{aligned} CVMO = 7V + 2 &= 8V - V + 2 \\ &= 8V - F + 2 \end{aligned}$$

I.e., X must equal 0.

Rule 4: For Bipyramids $X = 0$ (or 2) for Trigonal, $X = 1$ (or 3) for Tetragonal, and $X = 3$ for Pentagonal. In the PSEPT, bipyramids are examples of closo clusters with $7V + 1$ CVMO, and for these (and all deltahedra) $F = 2V - 4$; therefore

$$\begin{aligned} CVMO = 7V + 1 &= 8V - V + 1 \\ &= 8V - F - 2 \end{aligned}$$

I.e., $X = (F - 6)/2$. In this manner $X = 0$ for a trigonal bipyramid ($F = 6$), $X = 1$ for a tetragonal bipyramid ($F = 8$), etc. The possibility pointed out by Lauher[7] that some of these bipyramids may distort to accommodate $7V + 3$ CVMO's leads to the alternative values of X given in parentheses above.

Rule 5: $X = 1$ for a Trigonal Antiprism, $X = 1$ or 3 for a Square Antiprism, and $X = 3$ for a Pentagonal Antiprism. Therefore, the values of X in this rule reflect the designation of a trigonal antiprism (octahedron) as closo and a pentagonal antiprism as arachno and the ambiguous designation of a square antiprism either as closo derived from a dodecahedron by minor distortions[8] or as an arachno bicapped square antiprism.

Rule 6: $X = S$ for Vertex or Edge-Sharing (Connected) Polyhedra, Where S Is the Number of Shared Vertices or Edges, Respectively. Recently, the PSEPT approach has been extended to condensed polyhedral clusters.[9] For a pair of cubic polyhedra sharing a common vertex, it can be demonstrated[9] that CVMO $= 15(V + 1)/2 - 9$. For such polyhedra $V = 2F - 9$; therefore

$$\begin{aligned} CVMO &= \tfrac{1}{2}(16V - V - 3) \\ & \tfrac{1}{2}(16V - 2F + 6) \\ &= 8V - F + 3 \end{aligned}$$

I.e., $X = 1$, the number of shared vertices. A similar analysis leads to $X = 1$ for edge-sharing cubic polyhedra.

Given that nearly all polyhedral carbonyl clusters have electron counts between $14V - 4$ and $15V$, then only a limited number of topological variables must suffice for rationalizing the observed skeletal geometries. The PSEPT defines these topological variables in terms of the classes of polyhedra given in Table I. The "new topological electron-counting theory" utilizes many of the same classes of polyhedra, e.g. three connected polyhedra, capped polyhedra, and condensed polyhedra, but replaces the deltahedral class by bipyramids, pyramids, and antiprisms. Since the latter can generally also be described as closo, nido, and aracho deltahedra, this does not introduce a major new topological variable. The two approaches share common assumptions, have rules that are interconvertible, and lead to identical conclusions for the great majority of carbonyl cluster compounds.

Acknowledgment. Dr. B. K. Teo is thanked for sending me copies of his paper prior to publication.

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Contribution from AT&T Bell Laboratories,
Murray Hill, New Jersey 07974

TEC and SEP Electron-Counting Rules for Polyhedral Cluster Systems: Similarities and Differences, Strengths and Weaknesses

Boon K. Teo

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In the preceding paper, it is shown by Mingos that the newly developed topological electron counting[1-3] (TEC) approach is related, via Euler's theorem for polyhedra, to the widely used polyhedral skeletal electron pair theory[4-8] (PSEPT). In this paper,

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we wish to show that while the two approaches have some features in common, they also differ in many respects. A detailed discussion on their similarities and differences readily brings out the strengths and weaknesses of both approaches.

Similarities

There are several similarities between the TEC and the PSEPT methods. First, they both assume the effective atomic number (EAN) rule (explicit in TEC but implicit in PSEPT). Second, they both count the number of vertices. Third, both methods assume that there are three orbitals per vertex atom primarily responsible for cluster bonding. Fourth, both approaches assume that each polyhedral edge corresponds to a single-bond distance. (For clusters with vertex atoms that have the tendency to deviate from the EAN rule and/or with nonbonded or multiply bonded edges, it is necessary to modify both approaches accordingly.) Given these similarities, it is not surprising that the predictions are quite similar for certain types of clusters, including the deltahedral and the 3-connected polyhedral clusters.

Differences

Though the TEC and the SEP approaches have some features in common (cf. prceding section), they also differ in many important respects as outlined below:

Different Assumptions. While Euler's theorem is explicitly built into the TEC approach, the SEP or the PSEPT approach, in its simplistic beauty, does not require Euler's relation.

Different Theoretical Foundations. While the parameter X in the TEC scheme is related to the number of "missing" *antibonding* orbitals,[3] the skeletal electron pairs in the SEP approach can be given by the number of *bonding* orbitals.

Different Methodologies. While TEC counts the number of *faces*, SEP counts the number of *missing* vertices and *capping* atoms.

Different Formulas. While TEC needs only one equation (but with different X values) for all polyhedra, SEP requires different formulas for different types of polyhedra.

Different Ranges of Applicability. The TEC theory, in its present form, is not applicable to two-dimensional (planar, ring) clusters or clusters with more open structures (e.g. some arachno or hypho clusters). The PSEPT readily applies to these systems. On the other hand, the TEC approach readily applies to high-nuclearity clusters such as the square-antiprismatic $[Co_8C(CO)_{18}]^{2-}$[9] (see below), the face-to-face fused trioctahedron with one hidden edge $[Rh_{11}(CO)_{23}]^{3-}$[10] ($X = 3 \times 1$ (three octahedra) $- 1$ (hidden bond) $= 2$; with total number of electron pairs,[11] via eq 5b of ref 1, $T = 74$), the bidiminished ν_2 trigonal-bipyramidal $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$[12] ($X = 2 \times 1$ (two octahedra) $+ 3 \times 2$ (three trigonal bipyramids) $- 3$ (three hidden bonds) $= 5$; $T = 83$), the twinned-cuboctahedral $[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$[13] ($X = 1$; $T = 85$), and the pentacapped-cubic $[Rh_{14}(CO)_{25}]^{4-}$[14] ($X = 5$ for five caps, $T = 90$). New extension of the PSEPT approach can also be applied to these clusters (see preceding paper and ref 8).

Different Predictions. Even for closo deltahedra, one may sometimes find that the two methods differ in their predictions. As an example, the TEC approach[3] incorrectly predicted the number of skeletal electron pairs of an octadecahedron (e.g. $B_{11}H_{11}^{2-}$) to be 11, in contrast to the observed value of 12, which is correctly predicted by the PSEPT.

These differences in the basic assumptions, the theoretical foundations, the methodologies, the formulations, the ranges of applicabilities, and the predictive capabilities accent the *strengths* and *weaknesses* of both methods.

Conclusion

In summary, the TEC and the SEP (or its extended version, PSEPT) methods are similar in some respects but different in others. Each has its own strengths and weaknesses as discussed in the previous sections. The interrelationship between the two approaches can be simplistically summarized as

$$\text{TEC} \leftrightarrow \text{PSEPT} + \text{Euler} \qquad (1)$$

This equation recognizes the bridge—Euler's theorem—between the two methods. Even so, it is an oversimplification since the two methods are still not equivalent under Euler's theorem since they have different boundary conditions and capabilities as detailed in the preceding section.

It is important to recognize that both methods can be rationalized in terms of molecular orbital theory. In particular, the parameter X in the TEC approach is related to the number of "missing" *antibonding* cluster orbitals ($X = E - A$, where E is the number of edges and A is the number of antibonding orbitals)[3] whereas the number of skeletal electron pairs (B) in the SEP method is given by the number of *bonding* cluster orbitals. In this context, the two approaches are interconvertible but not equivalent.

The TEC approach allows for *multiple* electron counts for certain types of polyhedral clusters. This is important since metal cluster systems often exhibit multiple electron counts for the same geometry (with or without structural distortion), in contrast to boron hydride clusters where the electron counts are more uniquely defined for a given structure. For example, a trigonal-bipyramidal structure may have $X = 0$ as observed in $Os_5(CO)_{16}$[15] (72 electrons) or $X = 2$ as observed in $[Ni_5(CO)_{12}]^{2-}$[16] (76 electrons). Even more interesting is the square-antiprismatic structure, which is predicted by the TEC approach to have either $X = 1$ as observed in $[Co_8C(CO)_{18}]^{2-}$[9] (114 electrons) or $X = 3$ as observed in $[Ni_8C(CO)_{16}]^{2-}$[17] (118 electrons). Where multiple electron counts arise for a given structure, the PSEPT approach usually agrees with the higher electron counts predicted by the TEC method except for the trigonal bipyramid and octahedron, where the reverse is true.[18]

It is concluded that TEC and PSEPT are alternative yet complementary ways of electron counting for polyhedral cluster systems.

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