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The Enumeration of Electron-Rich and Electron-Poor Polyhedral Clusters

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We present as dual processes the capping of closed triangulated polyhedra with apical atoms and the making of holes in such polyhedra either by puncture of the surface or by excision of atoms and their edges. These processes are shown to generate stable chemical species containing respectively less or more than $2n+2$ skeletal electrons. The former species are designated as electron-poor whereas the latter are called electron-rich. Pólya's enumeration method is used to enumerate the distinct ways of capping and excising the closed, triangulated polyhedra to yield systems containing from four to twelve vertices. For the enumeration of cappings the appropriate cycle index is that of the dual of the polyhedron being capped, whilst for the enumeration of the excisions the cycle index is that of the polyhedron being excised.

Key words: Boranes – Carboranes – Polyhedral clusters – Pólya's enumeration theorem – Electron counts

1. Introduction

Closed, triangulated, polyhedral systems having an atom located at each of the n vertices are represented by the cage boron hydrides, the carboranes, and certain metal clusters. Such species are now well-known to be particularly stable if they contain $2n+2$ skeletal electrons [1–5]. In the present paper we propose a method for the enumeration of polyhedral systems containing more than $2n+2$ skeletal electrons, which we term "electron-rich", as well as one for polyhedral systems containing less than $2n+2$ skeletal electrons, which we term "electron-poor".

The electron-rich polyhedral systems have already been discussed in some detail in the literature, particularly in the case of the boron hydride derivatives [1, 3, 4]. In fact, there are now well-established families of *nido* compounds with $2n+4$

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skeletal electrons, and of *arachno* compounds with $2n+6$ skeletal electrons. If, in accordance with previous treatments [6], one considers only triangular faces to be closed faces, then nido compounds contain by definition one hole or non-triangular face. Arachno compounds, on the other hand, contain either two holes or one large bent hole. On this basis it may therefore be seen that the addition of electrons to a closed $2n+2$ triangulated polyhedron results in successive puncture of the surface to give holes with more than three edges. Alternatively viewed, the open polyhedral networks could arise from closed polyhedra by the excision of one or more vertices together with the edges terminating on them.

The properties of electron-poor polyhedral systems have been discussed by us in a recent paper [5]. Representatives of this class of compounds, which are much rarer than their electron-rich counterparts, may be considered either as triangulated polyhedra with one or more capped faces or as polyhedra containing tetrahedral chambers. Two actual examples of electron-poor polyhedral systems are the bicapped tetrahedral $Os_6(CO)_{18}$ (Ref. [7]) and the capped octahedral $Rh_7(CO)_{16}^{3-}$ (Ref. [8]), both of which contain $2n$ skeletal electrons.

In Table 1 we list certain closed, triangulated polyhedra having from four to twelve vertices. For the polyhedra containing seven, eight, ten, and eleven vertices two alternative closed polyhedra having differing symmetry elements are listed.[1] In each of these cases one of the polyhedra is found in cage boron hydrides and carboranes whilst the other is not. In the polyhedra with 7, 8, 10, and 11 vertices the unfavored polyhedra with n vertices can all be partitioned into a tetrahedron and a smaller, closed, triangulated polyhedron with $n-1$ vertices.

2. Enumeration of Capped and Excised Polyhedra

It has been shown [5] that complementary processes may be generated for the conversion of closed, triangulated polyhedra with n vertices, which require $2n+2$ skeletal electrons, into polyhedra characteristic of systems with either a larger or smaller number of skeletal electrons. For those systems having a larger number of skeletal electrons ($2n+4$ or greater), the appropriate process can be viewed either as polyhedral puncture in which holes, i.e. faces with more than three edges, are made resulting in the generation of new bonding orbitals but no additional electrons, or as polyhedral excision in which vertices together with all of their edges are removed so that more electrons are removed than bonding orbitals. We now demonstrate that the enumeration of possibilities for polyhedral excision and polyhedral capping by means of Pólya's Enumeration Theorem [10, 12] actually represent dual problems.

We consider first the enumeration of polyhedral excisions, starting from a closed, triangulated polyhedron with n vertices. The number of distinct nido systems that may be generated by excising one vertex from this polyhedron is equal to the number of orbits in this polyhedron. Similarly, the number of arachno systems that

[1] The enumeration of all polyhedra, even just those with triangular faces is a complex problem [9]. Table 1 is not exhaustive and contains only those with obvious symmetry elements.

Table 1. Some triangulated polyhedra and their duals

Polyhedron	Point group[a]	No. elements[b] v	e	t	Types of vertices[b] j_3	j_4	j_5	j_6	Found in boron cages	Dual polyhedron Name[c]	v	e	f
Tetrahedron	T_d/T	4	6	4	4	0	0	0	No	Tetrahedron	4	6	4
Trigonal bipyramid	D_{3h}/D_3	5	9	6	2	3	0	0	Yes	Trigonal prism	6	9	5
Octahedron	O_h/O	6	12	8	0	6	0	0	Yes	Cube	8	12	6
Pentagonal bipyramid	D_{5h}/D_5	7	15	10	0	5	2	0	Yes	Pentagonal prism	10	15	7
Capped octahedron	C_{3v}/C_3	7	15	10	1	3	3	0	No		10	15	7
D_{2d} dodecahedron	D_{2d}/D_2	8	18	12	0	4	4	0	Yes		12	18	8
Bicapped octahedron	D_{3d}/D_3	8	18	12	2	0	6	0	No		12	18	8
4,4,4-Tricapped trigonal prism	D_{3h}/D_3	9	21	14	0	3	6	0	Yes		14	21	9
4,4-Bicapped square antiprism	D_{4d}/D_4	10	24	16	0	2	8	0	Yes		16	24	10
3,3,4,4-Tetra-capped trigonal prism	C_{3v}/C_3	10	24	16	1	3	3	3	No		16	24	10
$B_{11}H_{11}^{2-}$ polyhedron	C_{2v}/C_2	11	27	18	0	2	8	1	Yes		18	27	11
Pentacapped trigonal prism	D_{3h}/D_3	11	27	18	2	3	0	6	No		18	27	11
Icosahedron	I_h/I	12	30	20	0	0	12	0	Yes	Pentagonal dodecahedron	20	30	12

[a] The first point group listed is the full point group. The second point group listed is the subgroup of the full point group consisting only of the proper rotations.

[b] The symbol v refers to the number of vertices, e to the number of edges, t to the number of triangular faces, f to the number of faces of any type, and j_n to the number of vertices of degree n. See: King, R. B.: J. Am. Chem. Soc. **91**, 7211 (1969).

[c] Only relatively familiar names for the dual polyhedra have been included.

may be generated by excising two vertices from this polyhedron may be determined by routine application of Pólya's method. The enumeration of double excisions is mathematically identical to the corresponding enumeration of disubstituted isomers. Furthermore, for systems with more than two holes analogous computational methods may be applied. For all of these enumerations the appropriate cycle index is that of the permutations of the vertices of the polyhedron.

Enumeration of polyhedral capping can be considered analogously. Starting again from a closed, triangulated polyhedron with n vertices, it is evident that the number of distinct systems that can be generated by capping one face is equal to the number of face orbits, i.e. the number of non-equivalent faces, in the polyhedron. The number of bicapped systems can also be obtained using Pólya's Theorem [10, 12]. This time, however, the appropriate cycle index is that of the permutations of the midpoints of the faces of the polyhedron. This index turns out to be identical to that for the permutations of the vertices of the dual polyhedron. Thus, the number of bicapped systems is the same as the number of disubstituted isomers of the dual polyhedron. In this sense, therefore, polyhedral excision and polyhedral capping may be seen to be dual operations, appropriate respectively to electron-rich and electron-poor systems.

3. The Counting Polynomials

We have evaluated the counting polynomials corresponding to the excised, triangulated polyhedra having from four to twelve vertices. The relevant cycle indices for the triangulated polyhedra, several of which have already been reported [11, 12], are given in Table 2. In order to differentiate between mirror

Table 2. Cycle indices for triangulated polyhedra and their duals

Polyhedron	Point group	Cycle index	Cycle index of dual
Tetrahedron	T	$\frac{1}{12}(x_1^4+8x_1^1x_3^1+3x_2^2)$	Self-dual
Tetrahedron	T_d	$\frac{1}{24}(x_1^4+8x_1^1x_3^1+3x_2^2+6x_1^2x_2^1+6x_4^1)$	Self-dual
Trigonal bipyramid	D_3	$\frac{1}{6}(x_1^5+2x_1^2x_3^1+3x_1^1x_2^2)$	$\frac{1}{6}(x_1^6+2x_3^2+3x_2^3)$
Trigonal bipyramid	D_{3h}	$\frac{1}{12}(x_1^5+2x_1^2x_3^1+3x_1^1x_2^2+4x_1^3x_2^1+2x_2^1x_3^1)$	$\frac{1}{12}(x_1^6+2x_3^2+4x_2^3+2x_6^1+3x_1^2x_2^2)$
Octahedron	O	$\frac{1}{24}(x_1^6+8x_3^2+3x_1^2x_2^2+6x_2^3+6x_1^2x_4^1)$	$\frac{1}{24}(x_1^8+6x_4^2+9x_2^4+8x_1^2x_3^2)$
Octahedron	O_h	$\frac{1}{48}(x_1^6+8x_3^2+7x_2^3+6x_1^2x_4^1+9x_1^2x_2^2+8x_6^1+3x_1^4x_2^1+6x_2^1x_4^1)$	$\frac{1}{48}(x_1^8+13x_2^4+12x_4^2+8x_1^2x_3^2+8x_2^1x_6^1+6x_1^4x_2^2)$
Pentagonal bipyramid	D_5	$\frac{1}{10}(x_1^7+4x_1^2x_5^1+5x_1^1x_2^3)$	$\frac{1}{10}(x_1^{10}+4x_5^2+5x_2^5)$
Pentagonal bipyramid	D_{5h}	$\frac{1}{20}(x_1^7+4x_1^2x_5^1+5x_1^1x_2^3+x_1^5x_2^1+4x_2^1x_5^1+5x_1^3x_2^2)$	$\frac{1}{20}(x_1^{10}+4x_5^2+6x_2^5+4x_{10}^1+5x_1^2x_2^4)$
D_{2d} dodecahedron	D_2	$\frac{1}{4}(x_1^8+3x_2^4)$	$\frac{1}{4}(x_1^{12}+3x_2^6)$
D_{2d} dodecahedron	D_{2d}	$\frac{1}{8}(x_1^8+3x_2^4+2x_1^4x_2^2+2x_8^1)$	$\frac{1}{8}(x_1^{12}+2x_4^3+3x_2^6+2x_1^2x_2^5)$
4,4,4-Tricapped trigonal prism	D_3	$\frac{1}{6}(x_1^9+2x_3^3+3x_1^1x_2^4)$	$\frac{1}{6}(x_1^{14}+2x_1^2x_3^4+3x_2^7)$
4,4,4-Tricapped trigonal prism	D_{3h}	$\frac{1}{12}(x_1+2x_3+3x_1x_2+4x_1x_2+2x_3x_6)$	$\frac{1}{12}(x_1^{14}+2x_1^2x_3^4+3x_2^7+x_1^6x_2^4+2x_2^1x_3^2x_6^1+3x_1^4x_2^5)$
4,4-Bicapped square antiprism	D_4	$\frac{1}{8}(x_1^{10}+2x_1^2x_4^2+x_1^2x_2^4+4x_2^5)$	$\frac{1}{8}(x_1^{16}+2x_4^4+x_2^8+4x_1^2x_2^7)$
4,4-Bicapped square antiprism	D_{4d}	$\frac{1}{16}(x_1^{10}+2x_1^2x_4^2+x_1^2x_2^4+4x_2^5+4x_2^1x_8^1+4x_1^4x_2^3)$	$\frac{1}{16}(x_1^{16}+2x_4^4+x_2^8+8x_1^4x_2^6+4x_8^2)$
$B_{11}H_{11}^{2-}$ polyhedron	C_2	$\frac{1}{2}(x_1^{11}+x_1^1x_2^5)$	$\frac{1}{2}(x_1^{18}+x_2^9)$
$B_{11}H_{11}^{2-}$ polyhedron	C_{2v}	$\frac{1}{4}(x_1^{11}+x_1^1x_2^5+x_1^3x_2^4+x_1^5x_2^3)$	$\frac{1}{4}(x_1^{18}+x_2^9+x_1^2x_2^8+x_1^4x_2^7)$
Icosahedron	I	$\frac{1}{60}(x_1^{12}+24x_1^2x_5^2+20x_3^4+15x_2^6)$	$\frac{1}{60}(x_1^{20}+24x_5^4+20x_1^2x_3^6+15x_2^{10})$
Icosahedron	I_h	$\frac{1}{120}(x_1^{12}+24x_1^2x_5^2+20x_3^4+16x_2^6+24x_2^1x_{10}^1+20x_6^2+15x_1^4x_2^4)$	$\frac{1}{120}(x_1^{20}+24x_5^4+20x_1^2x_3^6+16x_2^{10}+24x_{10}^2+20x_2^1x_6^3+15x_1^4x_2^8)$

image enantiomers and between geometrically different isomers, the cycle indices for both the full point groups and the proper rotation subgroups of the relevant triangulated polyhedra are also given in Table 2. The counting polynomials for the excisions are to be found in Table 3. In these polynomials, derived from the full point group of a triangulated polyhedron with n vertices, the coefficients of x correspond to the number of possible non-equivalent nido structures with $n-1$ vertices; the coefficients of x^2 correspond to the number of non-equivalent arachno structures with $n-2$ vertices. Comparison of the coefficients of the x and x^2 terms of a counting polynomial using the full point group and the proper rotation subgroup of a polyhedron on n vertices, allows one to identify the respective numbers of nido and arachno polyhedra (with respectively $n-1$ and $n-2$ vertices) which exist in pairs of distinguishable enantiomers because of the lack of a plane of symmetry or other improper rotation axis.

Interpretation of the coefficients of the higher powers of x in the counting polynomials derived from the cycle indices eventually runs into difficulties. As the number of possible species obtained by multiple excisions increases, problems arise in cases where either disconnected polyhedra are obtained or two non-equivalent excision sequences lead to the same highly open system. Such difficulties clearly do not occur with the single (x terms) and double (x^2 terms) excisions, which lead to the chemically significant nido and arachno species. In the present work our attention is focused mainly on the single and double excisions.

We have also evaluated the counting polynomials corresponding to the capped triangulated polyhedra with four to twelve vertices. Again, the relevant cycle indices for the duals of the triangulated polyhedra are given in Table 2. The counting polynomials for the cappings are presented in Table 3. In this latter case, there is no difficulty in interpreting the coefficients of the x^m terms in the counting polynomial derived from the full symmetry point group of the dual of a triangulated polyhedron on n vertices. These coefficients represent simply the number of different systems that can be obtained by capping m triangular faces. Moreover, comparison of the coefficients of the x^m terms of the counting polynomial of the dual of a given triangulated polyhedron when either the full symmetry point group or the pure rotation subgroup thereof is used allows the determination of the numbers of systems with m caps that exist as pairs of distinguishable mirror image enantiomers because of the lack of a reflection plane or other improper axis.

4. The Electron Counts

There are some limitations to the apparent duality of excision and capping in triangulated polyhedra. For example, there is a subtle difference between the effects of these two operations on the precise electron count required for the cluster. If an excision of a polyhedron with $n+1$ vertices is viewed as equivalent to puncture of a polyhedron with n vertices (as it is), then this puncture will generate precisely one new bonding orbital which will hold precisely two additional electrons. Thus, as discussed above, each puncture will generate the need for exactly two additional electrons to fill up all of the bonding orbitals. There will therefore be an orderly

Table 3. Counting polynomials for triangulated polyhedra and their duals

Polyhedron	Point group	Counting polynomial for excisions	Counting polynomial for cappings
Tetrahedron	T	$1+x+x^2+x^3+x^4$	$1+x+x^2+x^3+x^4$
Tetrahedron	T_d	$1+x+x^2+x^3+x^4$	$1+x+x^2+x^3+x^4$
Trigonal bipyramid	D_3	$1+2x+3x^2+3x^3+2x^4+x^5$	$1+x+4x^2+4x^3+4x^4+x^5+x^6$
Trigonal bipyramid	D_{3h}	$1+2x+3x^2+3x^3+2x^4+x^5$	$1+x+3x^2+3x^3+3x^4+x^5+x^6$
Octahedron	O	$1+x+2x^2+2x^3+2x^4+x^5+x^6$	$1+x+3x^2+3x^3+7x^4+3x^5+3x^6+x^7+x^8$
Octahedron	O_h	$1+x+2x^2+2x^3+2x^4+x^5+x^6$	$1+x+3x^2+3x^3+6x^4+3x^5+3x^6+x^7+x^8$
Pentagonal bipyramid	D_5	$1+2x+4x^2+5x^3+5x^4+4x^5+2x^6+x^7$	$1+x+7x^2+12x^3+26x^4+26x^5+26x^6+12x^7+7x^8+x^9+x^{10}$
Pentagonal bipyramid	D_{5h}	$1+2x+4x^2+5x^3+5x^4+4x^5+2x^6+x^7$	$1+x+5x^2+8x^3+16x^4+16x^5+16x^6+8x^7+5x^8+x^9+x^{10}$
D_{2d} dodecahedron	D_2	$1+2x+10x^2+14x^3+22x^4+14x^5+10x^6+2x^7+x^8$	$1+3x+21x^2+55x^3+135x^4+198x^5+246x^6+198x^7+135x^8+55x^9+21x^{10}+3x^{11}+x^{12}$
D_{2d} dodecahedron	D_{2d}	$1+2x+7x^2+10x^3+15x^4+10x^5+7x^6+2x^7+x^8$	$1+2x+12x^2+30x^3+72x^4+104x^5+128x^6+104x^7+72x^8+30x^9+12x^{10}+2x^{11}+x^{12}$
4,4,4-Tricapped trigonal prism	D_3	$1+2x+8x^2+17x^3+24x^4+24x^5+17x^6+8x^7+2x^8+x^9$	$1+3x+19x^2+62x^3+180x^4+335x^5+520x^6+576x^7+520x^8+335x^9+180x^{10}+62x^{11}+19x^{12}+3x^{13}+x^{14}$
4,4,4-Tricapped trigonal prism	D_{3h}	$1+2x+6x^2+12x^3+16x^4+16x^5+12x^6+6x^7+2x^8+x^9$	$1+3x+14x^2+41x^3+107x^4+193x^5+292x^6+322x^7+292x^8+193x^9+107x^{10}+41x^{11}+14x^{12}+3x^{13}+x^{14}$
4,4-Bicapped square antiprism	D_4	$1+2x+9x^2+16x^3+33x^4+34x^5+33x^6+16x^7+9x^8+2x^9+x^{10}$	$1+3x+20x^2+77x^3+246x^4+567x^5+1036x^6+1465x^7+1654x^8+1465x^9+1036x^{10}+567x^{11}+246x^{12}+77x^{13}+20x^{14}+3x^{15}+x^{16}$
4,4-Bicapped square antiprism	D_{4d}	$1+2x+7x^2+12x^3+22x^4+23x^5+22x^6+12x^7+7x^8+2x^9+x^{10}$	$1+3x+13x^2+49x^3+142x^4+315x^5+562x^6+785x^7+885x^8+785x^9+562x^{10}+315x^{11}+142x^{12}+49x^{13}+13x^{14}+3x^{15}+x^{16}$
$B_{11}H_{11}^{2-}$ polyhedron	C_2	$1+6x+30x^2+85x^3+170x^4+236x^5+236x^6+170x^7+85x^8+30x^9+6x^{10}+x^{11}$	$1+9x+81x^2+408x^3+1548x^4+4284x^5+9324x^6+15912x^7+21942x^8+21879x^9+21942x^{10}+15912x^{11}+9324x^{12}+4284x^{13}+1548x^{14}+408x^{15}+81x^{16}+9x^{17}+x^{18}$
$B_{11}H_{11}^{2-}$ polyhedron	C_{2v}	$1+5x+20x^2+52x^3+99x^4+108x^5+108x^6+99x^7+52x^8+20x^9+5x^{10}+x^{11}$	$1+6x+46x^2+216x^3+799x^4+2184x^5+4725x^6+8040x^7+11069x^8+12260x^9+11069x^{10}+8040x^{11}+4725x^{12}+2184^{13}+799x^{14}+216x^{15}+46x^{16}+6x^{17}+x^{18}$

Polyhedron	Point group	Counting polynomial for excisions	Counting polynomial for cappings
Icosahedron	I	$1+x+3x^2+5x^3+12x^4+14x^5+24x^6+14x^7+12x^8+5x^9+3x^{10}+x^{11}+x^{12}$	$1+x+6x^2+21x^3+96x^4+262x^5+681x^6+1302x^7+2157x^8+2806x^9+3158x^{10}+2806x^{11}+2157x^{12}+1302x^{13}+681x^{14}+262x^{15}+96x^{16}+21x^{17}+6x^{18}+x^{19}+x^{20}$
Icosahedron	I_h	$1+x+3x^2+5x^3+10x^4+12x^5+18x^6+12x^7+10x^8+5x^9+3x^{10}+x^{11}+x^{12}$	$1+x+5x^2+15x^3+58x^4+149x^5+371x^6+693x^7+1135x^8+1466x^9+1648x^{10}+1466x^{11}+1135x^{12}+693x^{13}+371x^{14}+149x^{15}+58x^{16}+15x^{17}+5x^{18}+x^{19}+x^{20}$

progression from $2n+2$ to $2n+4$, $2n+6$, etc. skeletal electrons as additional punctures are performed. However, the effect of capping on the number of electrons required for the capped polyhedron cannot be precisely defined since it depends upon the number of electrons donated by the cap. Thus, in $Os_6(CO)_{18}$ each $Os(CO)_3$ cap donates two electrons (i.e. 8 electrons from the osmium less the six electrons required for the three non-bonding lone pairs) whereas in $Rh_7(CO)_{16}^{3-}$ the $Rh(CO)_3$ cap donates three electrons (i.e. 9 electrons from the rhodium less the six electrons for the three non-bonding lone pairs). Consequently, there is no orderly progression of $2n+2$ to $2n$, $2n-2$, etc. skeletal electrons as the successive cappings are performed.

Another point to consider is that successive punctures or cappings lead to increased localization of the bonding in the cluster compounds. Each puncture splits the multi-center delocalized core molecular orbitals in the clusters into two molecular orbitals: one still in the core and one above the hole. This results in an increasing localization of the system. Similarly, addition of each cap increases the amount of the cluster that is contained in localized tetrahedra rather than delocalized larger polyhedra. Thus, excessive usage of either punctures or capping will lead to more localized systems that may lose many of the interesting properties, including the relatively high stability, characteristic of many of the closed triangulated polyhedral clusters containing $2n+2$ skeletal electrons. For this reason we believe that systems with large numbers of holes or caps are not well suited for treatment as perturbations on the closed triangulated polyhedra.

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