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Unification and Expansion of Wade-Mingos Rules with Elementary Number Theory

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ABSTRACT

The study of clusters by using the empirical formula $k = \frac{1}{2}$ (E-V) revealed the existence of cluster series. This gave rise to the design of a cluster table that has been highly refined to its current form in this paper. On closer scrutiny of the cluster table has further revealed an infinite number of cluster series based upon 4n for main group elements which obey octet rule and 14n for transition metal elements which obey the 18 electron rule. The cluster series decrease successively in valence electron count by 2 or increase successively by 2. The Wade-Mingos rules based upon 4n, 5n and 6n rules (polyhedral skeletal electron pair theory) all belong to the 4n-based cluster series of the cluster table are a subset of many series. This may simply be regarded as a unification and expansion of Wade-Mingos rules. The table is very simple to use to study clusters by students at secondary, undergraduate and postgraduate levels.

Key words: Wade-Mingos Rules, Elementary number theory.

INTRODUCTION

The Wade-Mingos rules have been exceedingly useful in the study of boranes, carboranes, main group element and transition metal carbonyl clusters for more than four decades¹⁻ ³. These rules are referred to as 4n, 5n, and 6n rules with which a geometry and cluster classification of a given cluster is determined. These rules refereed to as polyhedral skeletal electron pair theory (PSEPT) are now well known¹⁻³.

The Birth of the Empirical Formula $k = \frac{1}{2}$ (E-V)

While teaching a topic on Lewis structures of molecules at an undergraduate level, a desire to look for a simple formula that could assist students in drawing Lewis structures was mooted. In the search for the simple formula, N_2 diatomic molecule was considered first⁴. When the two N atoms are brought together to form the N_2 molecule with a triple bond, the two sets of five valence electrons are arranged in such a way that a triple bond is formed and each of the two N atoms then obeys the octet rule. By sheer intuition, it occurred that

doubling the octet electrons and subtracting the double valence electrons of N atom and then dividing by two, a value of 3 was obtained. This was the birth of the empirical formula $k = \frac{1}{2}$ (E-V) where E = 2x8 = 16, V = 2x5 = 10 and $k = \frac{1}{2}(16-10) = 3$. This meant that the formula gives us the triple bond that links up the N₂ atoms and by just inserting a lone pair on each N atom, a Lewis structure is constructed. What is fascinating is that the empirical formula simple as it is, is applicable to all diatomic and polyatomic systems whose atoms obey the octet rule. For instance, when the formula is applied to the diatomic species C_{a} (E= 16, V = 8, k = 4), CN⁺(E= 16,V = 4 +5-1 =8, k =4) , BN(E =16, V= 3+5 =8, k = 4), and $CB^{-}(E = 16, V = 4+3+1 = 8, k = 4)$ the value of k = 4 was obtained in agreement with the recent theoretical studies5. This observation that these diatomic species are held together by a quadruple bond underpins the power of the empirical formula.

Designing the Cluster Code

After determining the k values of many clusters, there was a need to design a label to distinguish them. In the case of N_a, we have two atoms (M-2), k value of 3 and a total of 10 valence electrons. But also in CO molecule, there are two atoms (M-2), k = 3 and 10 valence electrons. Therefore it made sense to label the diatomic molecules such as N₂ and CO as M-2-3-10. In the case of C₂ and its analogues, the label becomes M-2-4-8. Thus, a method for coding clusters was designed as M-x-k-V where M refers to the element in the cluster, k = number of bonds or linkages that hold the cluster system together and V is the total valence electrons of the cluster. When the C₂ with code M-2-4-8 is converted into C₂H₂ by adding two hydrogen atoms k becomes 3, that is, k = 3 the triple bond of acetylene H-CÎC-H. The two H atoms may be regarded as 'ligands' to the C₂ diatomic system. The code then changes to M-2-3-10 as in N_a. The method of calculating k value for lager clusters is the same. For instance, P_{4} [E = 4x8 = 32, V= 4x5 = 20, k = 1/2 (32-20) = 6, code M-4-6-20, tetrahedral]⁶, $B_{s}H_{a}$ [E = 5x8 = 40, V= 5x3+9 = 24, k = $\frac{1}{2}$ (40-24) = 8, code = M-5-8-24, square pyramid]⁷, B_cH_c²[E=5x8 =40, V =5x3+5+2 = 22, k =9, code M-5-9-22, trigonal bipyramid]⁶,andB₆H₆²[E=6x8 =48, V =6x3+6+2 =26, k = 11, code M-6-11-26, octahedral]6.In the case of transition metal carbonyl clusters, the same empirical formula will apply but

E= will refer to the total 18 electron system of the 'skeletal' atoms and V= the total valence electrons of metal atoms and all the ligands and any embedded atoms involved. Take the examples, $Mn_2(CO)_{10}[E = 2x18 = 36, V = 2x7+10x2 = 34, k = \frac{1}{2}$ (36-34) = 1, M-2-1-34]⁸, $Os_3(CO)_{12}[E = 54, V = 48, k = 3, M-3-3-48, triangle]^8$, $Ir_4(CO)_{12}[E = 72, V = 60, k = 6, M-4-6-60, tetrahedral]^8$, $Os_5(CO)_{16}[E = 90, V = 72, k = 9, M-5-9-72, trigonal bipyramid]^8$ and $Os_6(CO)_{18}^{-2}[E = 108, V = 86, k = 11, M-6-11-86, octahedral]^8$.

Origin of the Cluster Table and the Unification and Expansion of Wade-Mingos Rules

After analyzing the k values of many clusters, it was clear that the clusters follow a numerical sequence of numbers based on an alternating series of even and odd numbers. Hence, a cluster table was designed. Table 1 gives clusters ranging from two skeletal atoms (M-2) to ten (M-10). Ideally, the table can be extended in all directions.As you move down a column from the top, you traverse clusters of the same number of atoms M-x but different k values. For instance, we can move from M-2-4-8(C¹C) represented by say C₂ to M-2-3-10 (C) represented by N₂. Diagonal movement is simply a capping process in which k changes by 3 units("k = 3). For example movement from M-5-8-24[Fe₅(C)(CO)₁₄², square pyramid]⁹ to M-6-11-86-C[$Os_6(CO)_{18}^{2^\circ}$, octahedral]⁹ is a capping process. When this capping process or movement along the diagonal is carefully analyzed, it is discovered that it forms the basis upon which Rudolph's table is constructed¹⁰.An interesting constant ratio x:k:V =1:2:4 for main group elements and 1:2:14 for transition metal carbonyl clusters was identified for C¹C (monocapped) series. For instance, M-2-4-8, ratio is 1:2:4 and 2x4 =8, and also M-10-20-40 ratio is 1:2:4 and 10x4 =40 and so on. Clearly, this is the 4n series. In the case of the closo (C) series, M-2-3-10, n =2 and 4n+2 = 10 and M-6-11-26, n=6 and 4n+2 = 26. Clearly, this is 4n+2 series. It was readily discernible that all the main group element series were based upon 4n while those of the transition metal carbonyls based upon 14n (where n refers to the number of skeletal elements in the cluster). All the selected cluster series and their relationship to 4n and 14n are shown in the Table 1.It is fascinating that the widely used polyhedral skeletal electron paircluster seriessuch as 4n-2 (bicapped closo), 4n

	M-2	M-3 12	M-4 14	M-5 16	M-6 18	M-7 20	M-8 22	M-9 24	M-10 26	MG*	TM*
C7C		M-3-12-0 11	M-4-14-4	M-5-16-8 15	M-6-18-12 17	M-7-20-16 19	M-8-22-20 21	M-9-24-24	M-10-26-28 25	4n-12	14n-12
C°C	o	M-3-11-2	M-4-13-6	M-5-15-10	M-6-17-14	M-7-19-18	M-8-21-22	M-9-23-26	M-10-25-30	4n-10	14n-10
C ⁵ C	о М-2-8-0 7	M-3-10-4	M-4-12-8	M-5-14-12	M-6-16-16	00 M-7-18-20	M-8-20-24	M-9-22-28	24 M-10-24-28	4n-8	14n-8
C ⁴ C	, M-2-7-2 6	ج M-3-9-6 A	M-4-11-10	M-5-13-14	M-6-15-18	M-7-17-22	ы М-8-19-26 18	M-9-21-30	دی M-10-23-34 من	4n-6	14n-6
C³C	M-2-6-4	M-3-8-8	M-4-10-12	M-5-12-16	M-6-14-20	M-7-16-24	M-8-18-28	M-9-20-32	22 M-10-22—36	4n-4	14n-4
C2C	ы. М-2-5-6	M-3-7-10	ы М-4-9-14 о	M-5-11-18	M-6-13-22	M-7-15-26	M-8-17-30	M-9-19-34	M-10-21-38	4n-2	14n-2
C ¹ C	4 M-2-4-8 2	o M-3-6-12 E	о М-4-8-16 7	M-5-10-20	M-6-12-24	14 M-7-14-28	10 M-8-16-32	10 M-9-18-36	A-10-20-40	4n	14n
U	M-2-3-10	0 M-3-5-14	ر M-4-7-18	ы М-5-9-22	M-6-11-26	M-7-13-30	M-8-15-34	M-9-17-38	M-10-42	4n+2	14n+2
z	Z M-2-2-12	4 M-3-4-16	о М-4-6-20 Б	8 M-5-8-24 7	M-6-10-28	12 M-7-12-32	14 M-8-14-36	16 M-9-16-40	18 M-10-44	4n+4	14n+4
٨	- M-2-1-14	M-3-3-18	M-4-5-22	M-5-7-26	м-6-9-30 о	M-7-11-34	M-8-13-38	M-9-15-42	M-10-17-44	4n+6	14n+6
т	M-2-0-16	M-3-2-20	4 M-4-4-24	0 M-5-6-28	o M-6-8-32 ~	M-7-10-36	M-8-12-40	14 M-9-14-44	M-10-16-48	4n+8	14n+8
H-1		- M-3-1-22	о М-4-3-26	о М-5-5-30 Л	, M-6-7-34 e	ы М-7-9-38 о	M-8-11-42	M-9-13-46	M-10-15-50	4n+10	14n+10
Н-2		M-3-0-24	M-4-2-28	4. M-5-4-32	M-6-6-36	M-7-8-40	M-8-10-44	M-9-12-48	M-10-14-52	4n+12	14n+12
Н-3			1 M-4-1-30	з М-5-3-34	с М-6-5-38	M-7-7-42	9 M-8-9-46	M-9-11-50	13 M-10-13-54	4n+14	14n+14
H-4			5	м-5-2-36	4 M-6-4-40	o M-6-6-44	о М-8-8-48	M-9-10-52	M-10-12-56	4n+16	14n+16
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Table 1: Cluster Table for Main Group and Transition Metal arony

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M-G* = MAIN GROUP ELEMENT, TM* = TRANSITION METAL ELEMENT C= CLOSO, C'C = MONOCAPPED CLUSTER, C²C =BICAPPED,AND SO ON, N = NIDO, A = ARACHNO, H =HYPHO, H-1 =FIRST ROW BELOW, HYPHO, H-2 = SECOND ROW BELOW HYPHO, etc

(monocapped closo), 4n+2 (closo), 4n+4 (nido), 4n+6 (arachno) and 4n+8 (hypho) are inclusive as a subset of many series in Table 1. This tantamount to the unification and expansion of Wade-Mingos rules. Thus, on close examination, this table revealed the hidden natural law of the cluster series as follows: from the monocapped series, C¹C (4n) upwards, we have (4n-2) for bicapped series (C²C), (4n-4), (4n-6),(4n-8), (4n-10), (4n-12) and so on and downwards, (4n+2) for closo series (C), (4n+4) for nido series(N), (4n+6), (4n+8), (4n+10), (4n+12) and so on for main group element clusters. On the other hand for the corresponding transition metal carbonyl clusters we have for the monocapped cluster series C¹C (14n) andmoving upwards, we get (14n -2), (14n-4), (14n-6), (14n-8), (14n-10), (14n-12) and so on andmoving downwards in the table, the series (14n+2), (14n+4), (14n+6), (14n+8), (14n+10), (14n+12) and so on are obtained.

Categorizing a Cluster with the Cluster Table

Using the empirical formula $k = \frac{1}{2}$ (E-V) and the cluster Table 1, a given cluster can readily be categorized. For a example, $Rh_{e}(CO)_{16}[E = 6X18]$ = 108, V = 6X9+16X2 = 86, k = ½ (E-V) = ½ (108-86) = 11, M-6-11-86). By moving down the M-6 column reaching M-6-11-86, then moving across the row it is found that the cluster belongs to the closo (C) series M-6-11-86-C(14n+2) with an octahedral geometry⁸. Similarly, Rh₇(CO)₁₆³⁷(M-7-14-98) belongs to the monocapped series, C1C(14n)11.The capping is on an octahedral geometry which is diagonally below it in the closo (C) series. The complex,Os₈(CO)₂₂² has the cluster parameters[E = 8x18 =144, V= 8x8+22x2+2 = 110, k = ½ (E-V) = 1/2 (144-110) = 17, M-8-17-110]. Moving down the M-8 column until M-8-17-110, then moving across the row we encounter C²C. This means the complex is bicapped octahedral¹¹since it lies on the diagonal

Table 2: Correlation between Wade-Mingos and Cluster Table on Series

Cluster	W-M*	CT*	Electrons	W-М Туре	СТ Туре
Rh _c (CO) ₁₀	4n+2	4n+2	86(26 main group table)	С	С
Os (CO)	4n	4n	84 (24 main group)	C ¹ C	C¹C
Pb ₁₀ ^{2⁻}	4n+2	4n+2	42	С	С
Se ²⁺	4n+6	4n+6	22	А	А
B _z H ^{4⁻}	4n+4	4n+4	24	Ν	Ν
C ₈ H ₁	4n+6	4n+6	42	А	А
P, 13	5n	4n+4	20	-	Ν
P₄S	5n+3	4n+10	38	-	H-1
P₄O _c	5n+6	4n+16	56	-	H-4
S	6n	4n+16	48	-	H-4
$\mathring{C_{6}}H_{_{14}}$	6n+2	4n+14	38	-	H-3

W-M* = Wade-MINGOS, CT = Cluster table

where the closo (C) geometry below it is octahedral. The complex also belongs to the C²C cluster series (14n-2; 8x14-2 = 110). Another cluster, $Os_9(CO)_{24}^{2^{\circ}}$ has the following cluster parameters[E = 9x18 = 162, V = 9x8+24x2+2 = 122, k = 20, M-9-20-122]. By tracing M-9 column, the complex is found to belong to C³C(14n-4 ; 14x9-4 =122) series. This is a tricapped octahedral¹². Finally, the complex, $Os_{10}(CO)_{26}^{2^{\circ}}$ has the parameters[E = 180, V = 134, k = 23, M-10-23-134]. The cluster belongs to C⁴C(14n-6; 14x10-6 = 134) series. This is a tetracapped octahedral geometry¹¹ since it is diagonally above octahedral in the closo(C) series. The change in k value by 3 is characteristic of the capping process. For instance, k = 11 for octahedral(C), k = 11+3=14 for monocapped geometry (C¹C), k = 11+3+3 = 17 for bicapped geometry (C²C), k = 11+3+3+3 = 20 for tricapped geometry and k = 11+3+3+3=23 for tetracpped geometry (C⁴C).

Using the Cluster Table to Interpret some Literature work

Let us consider the following examples. The complex, $\operatorname{Felr}_4(\operatorname{CO})_{15}^{2^\circ}(1)$ and $\operatorname{Fe}_2\operatorname{Ir}_3(\operatorname{CO})_{14}(2)$ were found to have a trigonal bipyramid shapes but the former was more elongated in axial positions than the later¹³. The complex 1 has the cluster code M-5-7-76-A and 2 has the code M-5-9-72-C. The reason for this could be due to the fact the two complexes belong to different series. The complex $Os_{10}(CO)_{24}^{2^{-}}$ was described as having a tetracapped octahedral geometry¹³. The cluster parameters for the complex are [E = 180, V = 10x8+24x2+2 = 130, k = ½ (E-V) = ½ (180-130) = 25, M-10-25-130]. When we scan its diagonal below it, we encounter the following cluster code series: M-10-25-130(C6C)>M-9-22-118(C⁵C)>M-8-19-106(C⁴C)>M-7-16-94(C3C)>M-6-13-82(C2C). This means that the complex is not a tetracapped geometry based on an octahedral shape whose code is M-6-11-86(C) but rather on the geometry with a code M-6-13-82(C²C). The cluster that is tetracapped based on the octahedral geometry will have a value deduced as follows k = 11+3+3+3+3=23. This corresponds to a cluster code of M-10-23-134(C4C). As mentioned above, one such a cluster is Os₁₀(CO)₂₆²⁷ complex and not $Os_{10}(CO)_{24}^{2^-}$ complex. Thus, the cluster table could be of great assistance in understanding and re-interpreting some literature data.

The Cluster Table on CO stripping Experiments

The cluster table can be very helpful in understanding and appreciating the 'CO stripping' experiments. In this regard, McIndoe and his research teams have tremendously done a lot¹⁴⁻¹⁸. Their EDESI-MS studies have studied many carbonyl complexes¹⁴ including HOs₅(CO)₁₅, $PtRu_{5}(C)(CO)_{15}^{2}$, $Os_{10}(C)(CO)_{24}^{2}$, $Os_{17}(CO)_{36}^{3}$, $Co_{6}(C)(CO)_{15}^{2^{-}}, Pt_{3}Ru_{10}(C)_{2}(CO)_{32}^{2^{-}}, and Pd_{6}Ru_{6}$ (CO)24 . What is of great interest with EDESI-MS studies is that the decomposition intermediates of the initial cluster can be monitored by observing the peaks of the intermediate cluster species. For instance, HOs₅(CO)₁₅ was completely stripped naked by removal of all CO ligands to HOs, complex14. The initial cluster has the code M-5-9-72-C. It is likely to possess a trigonal bipyramid shape.During decomposition, for every loss of one CO ligand, the valence electrons decrease by two and the k value increases by one. Hence, the changes from HOs5(CO)15 toHOs may be expressed by the cluster code as follows: M-5-9-72-C> M-5-10-70>M-5-11-68>M-5-12-66>M-5-1364>M-5-14-62>M-5-15-60>M-5-16-58>M-5-17-56>M-5-18-54>M-5-19-52>M-5-20-50>M-5-21-48>M-5-22-46>M-5-23-44>M-5-24-42. It will be useful to investigate whether the completely naked cluster HOs₅⁻ could be isolated. This particular experiment could be considered as an example of a movement along the M-5 high way in the cluster table. The EDESI-MS studies vindicate the significance of the cluster table.

Correlation between the Cluster Table and Wade-Mingos Rules on Cluster Series

The cluster Table 1 analyzes a wide range of clusters for both main group elements and transition metals. It is therefore of great interest to find out how the table relates to Wade-Mingos rules of 4n, 5n and 6n. In this regard, it became necessary to use the cluster table approach to study some of the examples on which Wade-Mingos rules were applied. The examples tabulated below were taken from the website¹⁹. The selected examples are given in Table 2. As can be seen from Table 2, the cluster table approach arrives at identical series for monocapped series(4n), closo series (4n+2), nido series (4n+4) and arachno series (4n+6) as the Wade-Mingos rules. However, all the 5n series of Wade-Mingo rules in Table 2 have been found to fit in the Cluster Table 4n series. For instance, P, classified as a member of 5n by Wade-Mingos rules is found to be a member of 4n +4 (Nido) series. The P₄S₃ classified as 5n+3 under Wade-Mingos rules is a member of 4n+10 under the Cluster Table approach. For $P_4O_6(5n+6)$ under Wade-Mingos rules becomes 4n+16 under cluster table.S. becomes 6n under Wade-Mingos rules but is a member of 4n+16 under cluster table approach, and C₆H₁₄ is 6n+2 by Wade-Mingos approach but also a member of 4n+14 using the cluster table. Using the cluster table, the 4n-based series cover the clusters of the main group elements while the corresponding 14n-based series cover the clusters of the transition metal clusters.

CONCLUSION

The cluster table is a strong confirmation of Wade-Mingos rules. Furthermore, the table indicates that the clusters from small ones(M-2) to large clusters as (M-40) and bigger can be analyzed by the table in its present form which can be expanded as needed. All the clusters with skeletal atoms that obey either octet or 18 electron rule which can be analyzed by Wade-Mingos rules can also be readily categorized using the cluster table.The clusters of the main group elements whose systems obey the octet rule are based upon 4n series while the transition metal carbonyl clusters (skeletal elements must obey the 18 electron rule) are based on 14n series. The difference in electron count between corresponding series is 10n. By using the cluster k value and the cluster table, a cluster can be categorized. The cluster table for clusters can regarded in the same manner as the periodic table for elements. This approach of categorizing clusters is so easy that it could be taught to students in secondary school, undergraduate and postgraduate levels.

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