Progress on Electron Counting Rules of Clusters

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Abstract. The equations calculating the number of valence electrons on the boranes and heteroboranes are different from other simple condensed clusters such as the condensed organometallics and transition metal clusters. The equations calculating the number of valence electrons greatly differ between the condensed boranes and heteroboranes with the non-condensed boranes and heteroboranes too. These equations calculating the number of valence electrons on simple condensed clusters are all derived from the noble gas rule and Wade’s rule in the theory. The noble gas rule and Wade’s rule could be also applied to the high-nuclearity transition metal clusters, the equation details calculating the number of valence electrons is studied. The application ranges of the noble gas rule, Wade’s rule, and 6m+2n electron rule are extended. The calculating results are satisfying comparing with actual facts.

Introduction

The equations calculating the number of valence electrons for boranes, heteroboranes, and other clusters have many famous models and rules [1-3]. Mingos’ condensation rule suits to simple condensed transition metal clusters. The calculation results of Lauher’s rule [4] can be applied to various clusters. Teo’s C² model can be applied to the clusters of clusters such as vertex-, edge-, or face-sharing biocathedra and so on. Tang and Li’s structural rule and Jemmis’ mno rule, and Hofmann and Kiani’s abx rule can be employed in the boranes and heteroboranes. Wang and Schleyer’s 6m+2n electron rule could be obeyed by the “sea urchin” family boranes and carboranes. Mingos’ model, Teo’s extended Hume-Rothery rule and shell rule, Ciani and Sironi’s rule, Lauher’s EHHMO method, and Tang and Li’s model are approximate that could be used in the high-nuclearity transition metal clusters. These famous models and rules are all the fundamental theories for the clusters, and the syntheses of boranes, heteroboranes, and other clusters are key and important.

All Fragments Obey the Wade Rule in the Condensed Polyhedral Structure

The NVE is the number of valent electrons for any cluster. m is the number of individual polyhedral fragments. n is the number of main group atoms except the interstitial main group atoms, where, the valent orbitals in a main group atom doesn’t exceed four. Ni is the number of vertices for “i” individual closo-polyhedral fragment, \( \sum_{i} N_i \) is the total number of vertices form 1 to m closo-polyhedral fragments. \( v_b \) is the number of two-center two-electron bonds, or three-center two-electron bonds joined between two fragments. \( v_1 \) is the number of three-center two-electron bonds conjugated among three fragments, it is not discussed in text. \( \mu_0, \mu_1, \) and \( \mu_2 \) are the number of common main group atoms who are shared by two, three, and four fragments, respectively. n includes \( \mu_0, \mu_1, \) and \( \mu_2 \). Y is the number of non-skeletal electrons except the skeletal electrons in the non-common metal atoms. \( R_0, R_1, R_2 \) are the number of non-skeletal electrons in common metal atoms who are shared by two, three, and four fragments, respectively. \( T_0, T_1, \) and \( T_2 \) are the number of common metal atoms who are shared by two, three, and four fragments, respectively. Assuming that...
three valence orbitals in a common metal atom participate to form a fragment, thus, a common metal atom who are shared by two, three, and four fragments need six, nine, and twelve valent orbitals participating to form a polyhedral skeleton structures. The NOE is the number of valence electrons except that the number of valence electrons come from $v_0$, common main group atoms, and common metal atoms. $L_0$, $L_1$, and $L_2$ are the number of common edges who are shared by two, three, and four fragments, respectively. If "i" fragment obeys Wade’s rule, the skeletal valence electron pairs for "i" fragment are always equal to $N_i+1$. Assuming that all fragments obey Wade’s rule, we can obtain

$$\text{NOE} = 4v_0 + 16\mu_0 + 24\mu_1 + 32\mu_2 + 12T_0 + 18T_1 + 24T_2 + 2R_0 + 3R_1 + 4R_2 - 4L_0$$

$$-6L_1 - 8L_2 - 2n - 2\mu_0 - 4\mu_1 - 6\mu_2 - Y - 2R_0 - 3R_1 - 4R_2 = 2\sum_{i=1}^{m}(N_i + 1)$$

Because the following equation is true, we can have

$$NVE = \text{NOE} + 2v_0 + 8\mu_0 + 8\mu_1 + 8\mu_2 + 12T_0 + 18T_1 + 24T_2 + R_0 + R_1 + R_2 - 2L_0 - 2L_1 - 2L_2$$

The equation calculating the number of valence electrons for the condensed clusters including the condensed organometallics will change into

$$NVE = 2(n + \sum_{i=1}^{m}N_i + m - v_0 - 3\mu_0 - 6\mu_1 - 9\mu_2 + L_0 + 2L_1 + 3L_2) + Y + R_0 + R_1 + R_2$$

(1)

For a metal atom, $x$ is the number of valence orbitals occupied by valence electron pairs. $K$ is the total number of unpaired electrons. $M_0$ is the number of non-common surface metal atoms. Thereby, we will gain

$$Y + R_0 + R_1 + R_2 = 2[(x - 3)M_0 + (x - 6)T_0 + (x - 9)T_1 + (x - 12)T_2] + K$$

Where, $n_0$ is main group atoms outside fragments, it obeys the noble gas rule, $n$ includes $n_0$. The valence electron pairs per $n_0$ can’t exceed four. If the item $n_0$ exists, Eq. (1) will become into

$$NVE = 2n + 3n_0 + (x - 3)M_0 + \sum_{i=1}^{m}N_i + m - v_0 - 3\mu_0 - 6\mu_1 - 9\mu_2 + (x - 6)T_0 + (x - 9)T_1 + (x - 12)T_2 + L_0 + 2L_1 + 3L_2 + 1 + K$$

(2)

For a double bond, its $v_0$, $L_0$, $L_1$, or $L_2$ items will add one. Two conjugated carbon or boron atoms with a metal atom can form a three-center two-electron bond in boranes, heteroboranes, or organometallics. So that, it is rational that many carbon or boron atoms with a metal atom should form the most above-mentioned three-center two-electron bonds.

\[\text{Pb(C}_2\text{H}_5)_2\]
\[\text{U(C}_2\text{Me}_5)_3\text{Cl}\]
\[\text{B}_{13}\text{H}_{23}\]
\[\text{n-B}_{18}\text{H}_{22}\]
\[\text{Bi}_9\text{H}_{13}\]
\[\text{(AlMe)}_8\text{(CCH}_2\text{Ph)}_2\text{H}\]
\[\text{(CH}_2\text{)}_3\text{C}_2\text{B}_{12}\text{H}_{12}\]
\[\text{[Rh}_{17}\text{(CO)}_{30}^3\text{]}^3\text{+}\]
\[\text{[(Ph}_3\text{P)}_{10}\text{Au}_{13}\text{Ag}_{12}\text{Cl}_{6}](\text{SbF}_6)\]
\[\text{(MePh}_2\text{P)}_{10}\text{Au}_{12}\text{Ag}_{13}\text{Br}_9\]

\(\bigcirc\) is the pyramid or cone top atom. \(\blacktriangleleft\) is an atom shared by three pyramids. \(\times\) is the two-center two-electron skeletal bonds. \(\square\) is an atom shared by two pyramids.

Figure 1. The boranes, heteroboranes, organometallics, and transition metal clusters.
Pb(C\textsubscript{3}H\textsubscript{3})\textsubscript{2} can be viewed as a vertex-sharing pentagonal pyramid dimer (see Fig. 1) [1]. Pb is a common metal atom, whose oxidation number is +2. Its \( n, \, T\textsubscript{0}, \sum_{i=1}^{m} N\textsubscript{i}, \, m, \, x, \, K, \) and \( R\textsubscript{0} \) values are 10, 1, 14, 2, 6, 2, and 2, respectively. According to the equations (1,2), their \( NVE \) is all equal to 54, they are all the same as real observed value.

In U(C\textsubscript{3}Me\textsubscript{3})Cl (see Fig. 1) [1], U is a common metal atom, whose oxidation number is +4, its \( R\textsubscript{1} \) value of U atom is 3+1=4. Its \( n, \, T\textsubscript{1}, \sum_{i=1}^{m} N\textsubscript{i}, \, m, \, x, \, K, \) and \( R\textsubscript{1} \) values are 15, 1, 21, 3, 10, 2, and 4, respectively. According to Eq. (1), \( NVE=2(n+\sum_{i=1}^{m} N\textsubscript{i}+m+R\textsubscript{0})=82 \), it is in correspondence with the observed value. On the basis of Eq. (2), its \( NVE \) is also equal to 82.

It is surprised that \( B\textsubscript{15}H\textsubscript{23} \) [1] (see Fig. 1) seem to obey equations (1,2). \( B\textsubscript{15}H\textsubscript{23} \) is fused by one arachno-9-vertex family and one arachno-7-vertex family who shares a common vertex, its \( n, \sum_{i=1}^{m} N\textsubscript{i}, \, m, \) and \( \mu_0 \) values are 15, 20, 2, and 1, respectively. Therefore, \( NVE=2(n+\sum_{i=1}^{m} N\textsubscript{i}+m-3\mu\textsubscript{0})=68 \), it is in agreement with the observed value.

### The Condensation Rule for the Condensed Boranes and Heteroboranes

Tang and Li’s structural rule of boranes and heteroboranes could be written as follows

\[
NVE = 2(4n+9M + \sum_{i=1}^{m} F\textsubscript{i} + \mu\textsubscript{0} - v\textsubscript{0})
\]

(3)

Where, \( n \) is the number of main group atoms, \( M \) is the total number of transition metal atoms in which the unpair valence electrons and empty valent orbitals do not exist. \( F \) is defined as \( F=f+3(S+1) \), \( f \) is the number of triangular faces of a closo-borane and closo-heteroborane, thus, \( f=2N-4 \). \( S \) is the number of vertexes removed from (negative sign) or added to (positive sign) the corresponding closo-borane and closo-heteroborane, namely \( S=n+M-N \). So that, \( F=3(n+M)-N-1 \). Then, \( \sum_{i=1}^{m} F\textsubscript{i} = 3(\sum_{i=1}^{n} n\textsubscript{i} + \sum_{i=1}^{m} M\textsubscript{i}) - \sum_{i=1}^{m} N\textsubscript{i} - \sum_{i=1}^{m} 1 \). Where, \( \sum_{i=1}^{m} M\textsubscript{i} = M + T\textsubscript{0} + 2T\textsubscript{1} + 3T\textsubscript{2} \), \( \sum_{i=1}^{m} n\textsubscript{i} = n + \mu\textsubscript{0} \), \( \sum_{i=1}^{m} 1 = m \). Eq. (3) could be rewritten as follows

\[
NVE = 2(2n+6M + 3(\sum_{i=1}^{m} n\textsubscript{i} + \sum_{i=1}^{m} M\textsubscript{i}) - \sum_{i=1}^{m} N\textsubscript{i} - \sum_{i=1}^{m} 1)
\]

(4)

In Eq. (4) plus \( x, \, R\textsubscript{0}, \, R\textsubscript{1}, \, R\textsubscript{2}, \, Y, \, K, \) and \( n_0 \) item, the equations for calculating the number of valence electrons of condensed boranes and heteroboranes suggested by author are given by

\[
NVE = 2(n+3n_0 + \sum_{i=1}^{m} n\textsubscript{i} + m-v\textsubscript{0} - 2\mu\textsubscript{0}) + Y + R\textsubscript{0} + R\textsubscript{1} + R\textsubscript{2}
\]

(5)

\[
NVE = 2[n+3n_0 + (x-3)M\textsubscript{0} + \sum_{i=1}^{m} n\textsubscript{i} + m-v\textsubscript{0} - 2\mu\textsubscript{0} + (x-6)T\textsubscript{0} + (x-9)T\textsubscript{1} + (x-12)T\textsubscript{2} ] + K
\]

(6)

Where, \( M = M\textsubscript{0} + T\textsubscript{0} + T\textsubscript{1} + T\textsubscript{2} \). If the common metal-metal edges do not exist in the equations (3-6), the common edges made from main group atoms may be neglected for the condensed boranes and heteroboranes.

\( n\textsubscript{-}B\textsubscript{15}H\textsubscript{22} \) [1] is fused by two nido-10-vertex family who shares a common edge (see Fig. 1), its \( n, \sum_{i=1}^{m} N\textsubscript{i}, \, m, \) and \( \mu\textsubscript{0} \) values are 18, 22, 2, and 2, respectively. According to the equations (3-6), \( NVE = 2(n+\sum_{i=1}^{m} n\textsubscript{i} + m - 2\mu\textsubscript{0}) = 2(18+22+2-2×2) = 76 \), it is actual as fact.
Attentively, the fragments are all closo-, nido-, arachno-, hypho-structural boranes and heteroboranes in the equations (1-6).

The Condensation Rule for the Non-condensed Boranes and Heteroboranes

The “sea urchin” family boranes and carboranes disobey Tang and Li’s structural rule and Jemmis’ mno rule. They can be explained by Wang and Schleyer’s 6m+2n electron rule. Wang and Schleyer’s equation could be given by

\[
NVE = 2n + 6m + 2T = 2(n + 3m + T) \tag{7}
\]

Where, \(m\) is the number of individual pyramids in the skeletal structural surface. \(T\) expresses the number of polygons in the skeletal structural surface (attention, \(T\) is the number of trigons in the 6m+2n electron rule), and it does not belong to pyramids. For the “sea urchin” family boranes and carboranes, all main group atoms except tops of cones are common, thus, the equation (7) will become as follows

\[
NVE = 2(n + 3n_0 + \sum_{i=1}^{m} N_i + m + T - \nu_0 - 2\mu_0 - 3\mu_1)
\tag{8}
\]

Where, \(n\) is the number of main group atoms in the pyramids surface. The pyramids must be tetrahedron \((N_i=5)\), tetragonal pyramid \((N_i=6)\), pentagonal pyramid \((N_i=7)\), hexagonal pyramid \((N_i=8)\), and heptagonal pyramid \((N_i=9)\) in Eq. (8). The pyramids don’t include trigon, linear shape, and polygon. \(n_0\) is main group atoms outside pyramids. \(N_i\) is the total number of closo-polyhedral vertices form 1 to \(m\) pyramids. \(\nu_0\) is the number of 2-center 2-electron or 3-center 2-electron skeletal bonds joined among pyramids. \(\mu_0\) and \(\mu_1\) are the number of common main group atoms shared by two and three pyramids, respectively. \(n\) includes \(\mu_0\) and \(\mu_1\). Assuming that a polygon inner contains \(n-1\) dotted line, it will contain \(n\) false trigon, therefore, the “\(T\)” value of tetragon, pentagon, hexagon, and heptagon are still equal to one.

Applying the above-mentioned equations to non-condensed boranes and heteroboranes must obey the following rules: the top atoms of pyramid couldn’t be shared by other atoms, and other common atoms couldn’t be shared by more than three pyramids; if the number of \(\nu_0\) items are no less than three in a trigon or polygon, then, the “\(T\)” value of trigon or polygon will change into zero. In order to maximize the total bond energy for the non-condensed boranes and carboranes, firstly, the number of pyramids must be chosen the most; secondly, the sum of \(T\) values would be opted least; thirdly, the sum of \(\nu_0\) item is the most. The boranes and heteroboranes of octahedron or pentagonal bipyramid disobey Eq. (8).

Table 1. The electron count results for some non-condensed boranes and heteroboranes.

<table>
<thead>
<tr>
<th>Main group clusters</th>
<th>(n, n_0, \sum_{i=1}^{m} N_i, m, T, \nu_0, \mu_0,) and (\mu_1)</th>
<th>Calc.by (8)</th>
<th>Obs.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi_{9}^{+5}</td>
<td>9,0,18,3,2,0,6,0</td>
<td>40</td>
<td>40</td>
<td>[1]</td>
</tr>
<tr>
<td>(CH_{2})<em>{5}C</em>{2}B_{12}H_{12}</td>
<td>14,0,29,4,3,0,9,1</td>
<td>58</td>
<td>58</td>
<td>[1]</td>
</tr>
<tr>
<td>(AlMe)<em>3(CCH</em>{2}Ph)_3H</td>
<td>13,0,30,5,1,0,4,4</td>
<td>58</td>
<td>58</td>
<td>[1]</td>
</tr>
<tr>
<td>C_{2}B_{9}H_{13}</td>
<td>11,1,14,2,4,6,2,0</td>
<td>48</td>
<td>48</td>
<td>[1]</td>
</tr>
</tbody>
</table>

In the metal atoms, \(x\) is the number of valence orbitals occupied by valence electron pairs, \(K\) is the total number of unpaired electrons. For the non-condensed boranes and heteroboranes, we can gain
\[
NVE = 2(n + 3n_i + (x - 3)M_i + (x - 4)M_s + \sum_{i=1}^{m} N_i + m + T - \nu_0 - 2\mu_0 - 3\mu_i) + K
\]  

(9)

Where, \(M_i\) is the total number of surface metal atoms. \(M_s\) expresses the interstitial transition metal atoms. The interstitial transition metal atoms of icosahedra \([\text{Pt@Pb}_{12}]^{2-}\) and \([\text{Cd@Tl}_{12}]^{12-}\) [1] are Pt and Cd, respectively. They obey Eq. (9).

Attentively, the fragments are all the pyramids in the equations (7-9).

The Electron Counting Rules for High-nuclearity Transition Metal Clusters

The equation calculating the number of valence electrons for the various stable high-nuclearity transition metal clusters is as follows

\[
NVE = 2(4n_i + 9M_i - L_i + L_s + yM_i + Z) + K
\]

(10)

Where, \(n_i\) and \(M_i\) are the number of surface main group atoms and surface transition metal atoms, respectively. \(M_s\) includes capping transition metal atoms. \(L_s\) is the number of surface edges. A polyhedral structure could include many fragments. \(M_i\) is the number of the interstitial transition metal atoms connected by chemical bonds with other interstitial transition metal atoms. An interstitial transition metal atom is alone or buried in the fragments is indicated by \(M_{i0}\), which is only to be as electron donor. \(M_{i0}\) doesn’t belong to \(M_i\). \(M_i\) aren’t buried lone in the fragments \((Z > 0)\). If an interstitial atom lies in the pyramid top, it can’t constitute a pentagonal pyramid, hexagonal pyramid, or polygonal pyramid (vertices more than 6) with surface transition metal atoms. \(L_i\) is the number of edges made by \(M_i\) items. \(L_s\) couldn’t be made by \(M_{i0}\) with the other atoms. \(y\) is the coefficient of \(M_i, y\) is equal to 0 if chemical bonds don’t exist between \(M_i\) items; \(y = 1\) if chemical bonds exist between \(M_i\) items. \((NVE)_W\) is the number of valence electrons obtained from Wade’s rule or Lauher’s EHMO method, and \((NVE)_L\) is the number of valence electrons obtained from the noble gas rule, \((NVE)_W\) minus \((NVE)_L\) are equal to 2\(Z\). The total “\(Z\)” value of fragments must be chosen to be the most in the clusters. The fragments have to be closo- or nido- cage structures and other cage structures such as the pyramids, bipyramids, prisms, antiprism, some cage fragments, see Fig. 2. The fragments can share vertex, line, trigon, butterfly, and polygon with other fragments, but calculating \(Z\) value can’t be repeated. \(K\) is the number of unpair valence electrons. \(CVMO\) is the number of cluster valence molecular orbitals. If a transition metal atom has empty valent orbitals or \(CVMO\) is more than nine, the coefficient value of \(M_i\) and \(M_s\) will be reduced or added. \(O\) is the number of empty valent orbitals or \(CVMO\) which is more than nine. The hidden edges express the edges buried in inner. The hidden edges except \(L_i\) and \(L_s\) items only are to be as electron donors and not as part of the polyhedral structure. \(L_i\) and \(L_s\) don’t include the hidden edges. \(n_i\) doesn’t include the interstitial or capping main group atoms as well as hydrogen atoms, they are all only to be as electron donors. \(n_i\) must participate to consist of a fragment \((Z > 0)\), if an interstitial transition metal atom \(M_{i0}\) is buried in this fragment (moreover, \(M_i\) is seldom, and \(n_i\) is much), \(M_{i0}\) will be similar to \(M_i\), but the coefficient of \(M_{i0}\) will become into \(x-4\).

Table 2. Applications of Eq. (10) to some high-nuclearity metal clusters.

<table>
<thead>
<tr>
<th>Clusters</th>
<th>(M_i)</th>
<th>(L_i, M_s, Z), and (y)</th>
<th>Obs.</th>
<th>Counted by Eq. (10) and Mingos</th>
<th>Prediction of (K) and (O) values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}<em>{17}(\text{CO})</em>{30}]^{3-})</td>
<td>16,40,0,0,4,0</td>
<td>216</td>
<td>216,216</td>
<td>0.0</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>([\text{Ph}<em>3\text{P}]</em>{10}\text{Au}<em>{13}\text{Ag}</em>{12}\text{Cl}_4\text{(SbF}_6\text{)})</td>
<td>22,55,0,1,14,0</td>
<td>314</td>
<td>314,314</td>
<td>0.0</td>
<td>[1]</td>
<td></td>
</tr>
<tr>
<td>((\text{MePh}<em>2\text{P})</em>{10}\text{Au}<em>{12}\text{Ag}</em>{13}\text{Br}_9)</td>
<td>22,60,0,21,0</td>
<td>318</td>
<td>318,318</td>
<td>0.0</td>
<td>[1]</td>
<td></td>
</tr>
</tbody>
</table>

In Table 2, \([\text{Rh}_{17}(\text{CO})_{30}]^{3-}\) contains four octahedra, \([\text{Ph}_3\text{P}]_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8\text{(SbF}_6\text{)}\) contains two icosahedra, \((\text{MePh}_2\text{P})_{10}\text{Au}_{12}\text{Ag}_{13}\text{Br}_9\) contains three icosahedra, see Fig. 1.
Summary

For a fragment, \( n, M, L, \) and \( N \) are the number of surface main group atoms, surface transition metal atoms in which the unpair valence electrons and empty valent orbitals do not exist, surface edges, and closo-polyhedral vertices, respectively. The equation of Wade’s rule can be given by \( NVE = 2(CVMO) = 2(n + 6M + N + 1) \), and the noble gas rule can be given by \( NVE = 2(4n + 9M - L), N = [NVE - 2(n + 6M + 1)]/2 = [(CVMO) - (n + 6M + 1)] \). Where, \( M \) and \( n \) do not include interstitial atoms.

The \( R_0, R_1, \) and \( R_2 \) value of common atoms are relation with the number of empty valent orbitals, unpair electrons, structure, atomic oxidation number and coordination number of transition metal atoms. Many messages of common atoms can be guessed from the \( R_0, R_1, \) and \( R_2 \) value.

The equations \((1, 2, 5, 6, 9, 10)\) have predictive effect, they are interesting structural rules. Assuming that the high-nuclearity transition metal clusters have two kinds of skeletons, that is, the surface skeleton and inner skeleton. The inner skeleton are made from the part of \( M_i \) items and \( L_i \) items, which don’t offer valence electrons to surface skeleton. Therefore, \( M_i \) items and \( L_i \) items must be added to Eq. \((10)\). The hidden edges and \( M_{io} \) don’t participate to generate two kinds of skeletons, only are to be as electron donors and not as part of the polyhedral skeletons. Therefore, the hidden edges and \( M_{io} \) items should not appear in Eq. \((10)\). Eq. \((10)\) can easily explain many exceptional cases. Eq. \((10)\) bases on the noble gas rule and Wade’s rule, and can be apply to many types of clusters. The same single covalent bond length varying 10% ~ 15% is reasonable. When the number of transition metal atoms reach 50, the count results of Eq. \((10)\) will be higher comparing with the observed value, this shows that the bonding capability for \( p \) and \( d \) valence orbitals of transition metal atoms all becomes weaker.

References


