Electron-Orbital Counting Rules and Bonding Topology

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1. Introduction

When discussing the structure of a discrete chemical species, the necessary data may be divided into four distinct levels:

1) Stoichiometric Composition

2) Molecular Composition

3) Bonding Topology

4) Molecular Configuration (Geometry)

The first of these gives the empirical formula for a species; the second, requiring a knowledge of the molecular weight, gives the molecular formula for a species; the third, involving the concept of valence, gives a two-dimensional mapping of the bonding within a species; and the fourth gives the species' three-dimensional shape.

The above levels roughly reflect the historical order in which different aspects of chemical structure became accessible to the chemist. Well into the 19th century stoichiometric composition was the only unambiguous molecular parameter available. Then around 1860 molecular composition was put on a firm basis as a result of Cannizzaro's reaffirmation of Avogadro's hypothesis and the validity of physical methods (i.e., gas densities) for determining molecular weight. This was followed in rapid succession by the rise of the concept of valence (Couper, Kekulé, Butlerov, and. Frankland) and postulation of the tetrahedral carbon atom by van't Hoff and Le Bel. By the end of the 19th century Werner had added the pyramidal nitrogen atom and the octahedral, tetrahedral, and square planar structures of metal complexes to the list of stereochemical postulates, all of these being brilliantly confirmed by the discovery of X-ray diffraction techniques in this century.

Simple qualitative rules for predicting molecular geometry have received a great deal of attention at the textbook level. Outstanding examples are the Goldschmidt radius-ratio rules for ionic solids (l), the Gillespie Valence-Shell Electron-Pair Repulsion Rules (VSEPR) (2), and Wade's electron-counting rules for electron-deficient cluster species (3). In general, the prediction of information at any of the above four levels requires a knowledge of all the levels preceding it in the list. Thus we cannot predict the bonding topology, in the form of a Lewis dot structure, for example, without first knowing the molecular formula. Similarly, rules for predicting molecular geometry always require a knowledge of the bonding topology. The VSEPR rules require a Lewis dot structure as input data and Wade's rules require a knowledge of which atoms form the cluster and which act as external ligands.

However, despite the fact that geometry rules are generally dependent on a knowledge of the bonding topology, the qualitative rules which are used to predict such topologies seldom receive systematic treatment in the textbook. Instead, we have a collection of special rules, valid only for certain classes of compounds, which are scattered throughout the chemistry curriculum. These range from the octet rule and Lewis dot structures of elementary chemistry to the *styx* rules and the generalized *8-N* rule (which we call the *8-G* rule) of inorganic chemistry and solid-state chemistry.

The purpose of this review is to collect all of these qualitative topology rules together and to demonstrate that they are all special cases of a general electron-orbital counting procedure. It is not necessarily recommended that the resulting equations should be used as a set of memorized "rules" when teaching this subject to students. All that is intended is that we as teachers better understand the interrelations and limitations of the material we teach. Our approach will be similar to that originally given by Bent (4).

2. Hybrid Molecular Orbital Topologies

We begin by generalizing the Lewis dot description of molecules and ions so as to include not only the lone pairs (i.e., one-center, two-electron or lc-2e components) and two-center, two-electron (2c-2e) bonds of traditional Lewis structures, but the possibility of other multicentered, multielectron components as well, such as the 3c-2e bonds found in the boron hydrides. Following the suggestion of Carpenter (5), conjugated π-electron systems will also be represented as single multicentered bonding components, the π-system in benzene, for instance, being thought of as a 6c-6e component.

We call this the hybrid molecular orbital (MO) description because it represents a mixture of localized

and delocalized MO's – the lc-2e, 2c-2e, and closed yc-2e components corresponding to localized MO's and the open yc-xe components to delocalized MO's. This description is actually used in most textbooks as the σ-bonds generally shown for such molecules as benzene are in fact localized MO's and not the true delocalized canonical MO's for the sigma bonding system, whereas the π-system is usually represented in terms of delocalized MO's rather than in terms of an equally valid localized MO description (6).

Using this approximation, we assume the existence of the following numbers and kinds of bonding components:

U_0 = number of lc-0e components

U_l = number of lc-le components

U_2 = number of lc-2e components

B_0 = number of 2c-0e components

B_l = number of 2c-le components

B_2 = number of 2c-2e components

M_x = number of yc-xe components (where y > 2 and x = 0, 1, 2, 3, ... up to x < 2y).

The first component corresponds to an empty valence orbital localized on a single center or atom, the second to the same orbital singly occupied, the third to a lone pair, etc. Likewise, B_2 refers to the number of two-center, two-electron bonds, B_l to the number of two-center, one-electron bonds, etc. M_x is the number of some generalized y-center, x-electron bond.

The restriction that x < 2y is a result of assuming that each center contributes only one atomic orbital (AO) to the delocalized multicentered bonding component. Hence, the total number of MO's formed equals the total number of centers involved and, when x = 2y, all of the MO's, both bonding and antibonding, will be occupied, leading to a net nonbonding component.

We now make the following electron and orbital counts:

Electron Count

$$E = U_l + 2U_2 + B_l + 2B_2 + xM_x$$

Orbital Count

$$O = U_0 + U_l + U_2 + 2B_0 + 2B_l + 2B_2 + yM_x$$

where E is the total number of valence electrons in the species, O is the total number of valence atomic orbitals in the species, and we have assumed only one kind of multicentered component per species.

These equations may be simplified if we restrict ourselves to stable, long-lived species. Experience shows that these usually have closed-shell structures (Lewis, 1916) (7) and no empty valence orbitals (Pitzer, 1953) (8). Therefore, we can eliminate U_0, B_0, M_0, B_l, U_l and M_x for x an odd number:

$$E = 2U_2 + 2B_2 + xM_x$$

$$O = U_2 + 2B_2 + yM_x$$

Simultaneously solving these equations for U_2 and B_2 gives:

$$U_2 = (E - O) + (y - x)M_x \tag{1}$$

$$B_2 = (O - E/2) + (x/2 - y)M_x \tag{2}$$

If we further restrict ourselves to main-block elements and assume only s- and p-orbital participation, then:

$$O = 4N + n \tag{3}$$

where N is the number of heavy atoms in the species and n is the number of hydrogen atoms. Substitution into equations 1 and 2 gives:

$$U_2 = E - (4N + n) + (y - x)M_x \tag{4}$$

$$B_2 = (4N + n) - E/2 + (x/2 - y)M_x \tag{5}$$

as the final set of topological equations for the hybrid MO description.

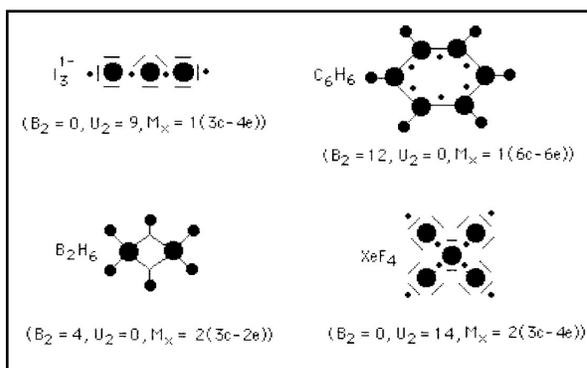Unhappily, given only E and O, these equations cannot be uniquely solved for B_2 and U_2 since we have

Figure 1. Example topologies illustrating the use of equations 4 and 5.

only two relations but five unknowns (U_2, B_2, M_x, y and x). However, in order to demonstrate the validity of the equations some example topologies are given in figure 1 using generally accepted values of M_x, y and x. This is, of course, one of the qualitative drawbacks of the hybrid MO description. By allowing for the existence of multicentered bonding components so much flexibility is introduced that it is no longer possible to deduce a unique set of bonding components merely by the expediency of counting electrons and orbitals.

3. Valence Bond Topologies

The difficulties associated with obtaining unique solutions to equations 4 and 5 did not arise in Lewis' original formulation of his electron-pair bond because the use of multicentered bonding components was not recognized at the time. As a result there were many species for which Lewis structures could not be written. Luckily, however, this restriction was valid for most organic compounds and the success of Lewis structures in this area insured their acceptance as a useful chemical concept.

These limitations were also carried over in the valence bond (VB) approach, where situations which require multicentered components in the hybrid MO approach are instead described using a weighted superposition or resonance of limiting structures composed of only 1c-2e and 2c-2e components. Removal of the yc-xe components reduces equations 4 and 5 to:

$$U_2 = E - O = E - (4N + n) \qquad (6)$$

$$B_2 = O - E/2 = (4N + n) - E/2 \qquad (7)$$

These equations are capable of unique solution for a given set of E and O values and give topologies corresponding to our conventional Lewis dot structures. Indeed, equation 7 was originally derived by Langmuir in 1919 as an expression of the octet rule (9). Some
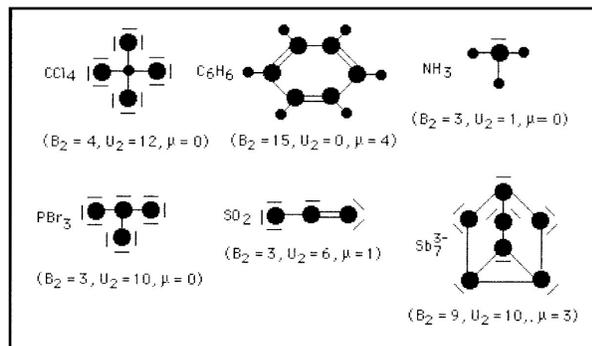

Figure 2. Example VB topologies illustrating the use of equations 6 and 7.

example topologies are given in figure 2. They may be unique for certain species (e.g., CCl_4) or correspond to one of several possible resonance structures for others (e.g., C_6H_6).

Figure 3 summarizes the minimum number of 2c-2e components needed to establish complete VB connectivity for several classes of structures. The results of this table may be combined with equation 7 to give
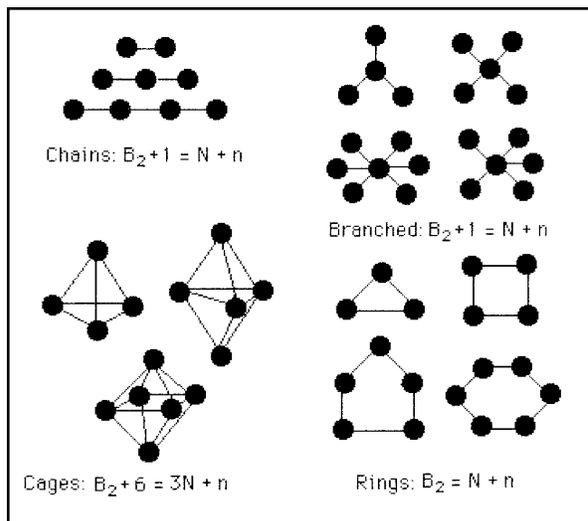

Figure 3. VB connectivity requirement for simple topologies.

information about the number of 2c-2e components involved in multiple bonds. Using the notation $B_{2\sigma}$ and $B_{2\pi}$ as convenient labels for the number of 2c-2e sigma and pi bonds respectively, equation 7 may be rewritten as:

$$B_{2\sigma} + B_{2\pi} = (4N + n) - E/2 \qquad (8)$$

Figure 3 shows that for linear and branched structures:

$$B_{2\sigma} = N + n - 1$$

Substituting this into equation 8 and solving for $B_{2\pi}$ gives:

$$B_{2\pi} = 3N + 1 - E/2 \qquad (9)$$

as the number of 2c-2e components involved in multiple bonds beyond those in the primary sigma framework. This result was originally obtained by Lever (10, 11) and similar substitutions may be made for ring and cage structures.

Actually the result in equation 9 may be derived in a more general form by means of graph theory (12). For any graph composed of n_v points (i.e., vertices) and

n_e connecting lines (i.e., edges), graph theory defines a number, μ, known as the *cyclomatic* number of the graph:

$$\mu = n_e - n_v + 1 \tag{10}$$

which represents the number of independent closed loops or cycles in the graph. Graph theory can be made isomorphous with VB topology by equating vertices with atoms, edges with bonds, and cycles with either rings or multiple bonds (considered to be two-sided rings). Substitution of these identities and the result in equation 7 into equation 10 gives:

$$\mu = B_2 - (N + n) + 1$$

$$\mu = (4N + n) - E/2 - (N + n) + 1$$

$$\mu = 3N + 1 - E/2 \tag{11}$$

This is. of course, the same as the result as in equation 9 but now has the general interpretation that μ represents the number of multiple bonds or rings for any class of structures composed of 2c-2e bonds.

The use of equation 11 can be illustrated by applying it to the class of alkanes using its generalized composition formula C_xH_{2x+2}. Rewriting equation 11 in terms of x, gives:

$$\mu = 3x + 1 - (4x + 2x + 2)/2 = 0$$

thus confirming that the alkanes as a class do not contain multiple bonds or rings in their VB topologies. Similar substitutions for the simple alkenes, C_xH_{2x}, and alkynes, C_xH_{2x-2}, give $\mu = 1$, and $\mu = 2$, respectively, in keeping with the presence of double (one cycle) and triple (two cycles) bonds in these species.

Much of the research of the last 50 years has been directed toward understanding the bonding in those species which violate the conditions set by equations 6 and 7, and in fact, as will be demonstrated in the following sections, these equations can be used to derive explicit conditions for the existence of such *electron-rich*, *electron-deficient*, and *orbital-rich* species.

4. Electron-Rich Species

When the cyclomatic number of a graph is less than 0, the graph is disconnected, that is, one or more of the vertices will be isolated or not connected to the rest of the graph. In terms of VB topology this would correspond to a no-bond situation. Hence, by equation 10, the necessary condition for a discrete species having a completely connected VB topology is that $\mu \geq 0$ or:
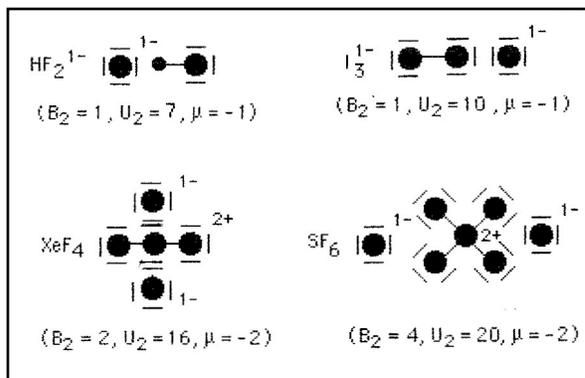

Figure 4. Example topologies illustrating the "no-bond" resonance structures obtained by applying equations 6 and 7 to electron-rich species

$$B_2 + 1 \geq N + n$$

Substituting this into equation 7 then gives:

$$E \leq 6N + 2$$

as the necessary condition for complete connectivity using only 2c-2e and lc-2e components.

When $E = 2O$, equations 6 and 7 give a value of zero for B_2 and a value of $4N + n$ for U_2. This corresponds to all of the isolated atoms having completely filled valence shells, that is, to a nonbonding situation. Thus, species having a total number of valence electrons lying between the limits:

$$8N + 2n > E > 6N + 2 \tag{12}$$

are "electron-rich" in the sense that they have too many electrons to have complete VB connectivity but too few to prevent some kind of chemical interaction.

Classic examples of this kind of species are I_3^- and HF_2^- and use of equations 6 and 7 leads to "no-bond" resonance structures like those in figure 4. In the hybrid MO representation, on the other hand, a multicentered 3c-4e component is used, as shown in figure 1 for I_3^-.

Another way out of this dilemma is to "expand the octets" of the constituent atoms and so increase the value of O. If we let the number of AO's per heavy atom, i, be a variable Z_i instead of 4, then equation 12 becomes:

$$2(\Sigma Z_i + n) > E > 2(\Sigma Z_i - N + 1)$$

and by altering Z_i accordingly E can always be made to fall within the limits of electron-precise compounds. We will consider the validity of octet expansion in the final section.

5. Electron-Deficient Species

When $E < O$ equation 6 gives a negative value for U_2, which is physically absurd. Such species are electron deficient. The problem can only be removed by returning to equations 4 and 5 and invoking some type of multicentered bonding component or by returning to the original orbital and electron counts and relaxing the condition that we are dealing with closed shell species with no empty valence orbitals. This latter step would allow one to prevent negative values of U_2 by invoking lc-0e, 2c-0e, or 2c-le components and the corresponding versions of equations 6 and 7 would become:

$$U_2 = (E - O) + U_0 + 2B_0 + B_l \qquad (13)$$

$$B_2 = (O - E/2) - U_0 - 2B_0 - 3B_l/2 \qquad (14)$$

Structures generated in this manner correspond to "no-bond" resonance structures containing either empty valence orbitals or unpaired electrons. Thus diborane, with U_0 as the only additional term in equations 13 and 14, gives:
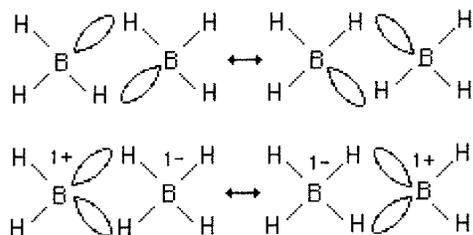
Chemical experience, however, has shown that the first alternative is preferable. By "extending" the VB description so as to include 3c-2e components, Lipscomb and coworkers have shown that one can successfully treat the VB topologies of both the boron hydrides and carboranes (13). Returning to equations 4 and 5 and setting $M_x = T_2$, (where $y = 3$, $x = 2$), gives:

$$U_2 = E - O + T_2 \qquad (15)$$

$$B_2 = O - E/2 - 2T_2 \qquad (16)$$

As we are invoking the minimum number of 3c-2e components required to prevent U_2 from becoming negative, that is, only enough to maintain U_2 at zero, we are now able to explicitly solve equation 15 for T_2:

$$T_2 = O - E \qquad (17)$$

which, on substitution into equation 16 gives:

$$B_2 = 3E/2 - O \qquad (18)$$

Thus we still have a set of equations capable of unique solution for a given set of E and O values. The validity of equations 17 and 18 is shown for some example boron hydrides in figure 5. Additional examples may be obtained by comparing the results of the equations with the VB and localized MO boron hydride topologies given by Lipscomb in references 13 and 14.
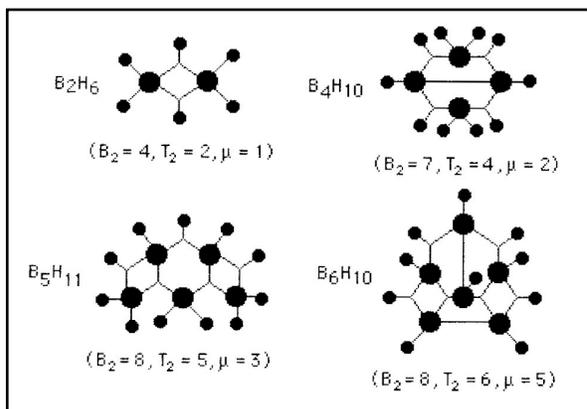

Figure 5. Example boron hydride topologies illustrating the application of equations 17 and 18.

Because the boron hydrides form a class of compounds, all of which may be represented by the general formula $[B_pH_{p+q+c}]^c$, it is possible to make the informational content of equations 17 and 18 more explicit. Assume that only the following components are found in this class of compounds:

p = number of 2c-2e B-H bonds = B atoms = normal terminal H atoms (i. e., one per B atom).

q = number of additional H atoms beyond those in p.

c = net charge = number of protons added or subtracted.

s = number of 3c-2e B-H-B bonds.

t = number of 3c-2e B-B-B bonds.

y = number of 2c-2e B-B bonds.

x = number of additional 2c-2e B-H bonds beyond those in p.

Substituting the proper components into equation 17 (remember protons contribute orbitals but no electrons, whereas H atoms contribute both) gives:

$$T_2 = O - E$$

$$s + t = (4p + p + q + c) - (3p + p + q)$$

$$s + t = p + c \tag{19}$$

Substituting the proper components in equation 18 gives:

$$B_2 = 3E/2 - O$$

$$y + p + x = 3(3p + p + q)/2 - (4p + p + q + c)$$

$$y + p + x = p + q/2 - c \tag{20}$$

In addition, we may do a purely stoichiometric balance of the hydrogen content:

$$s + x = q + c \tag{21}$$

Solving equation 21 for x gives:

$$x = q + c - s$$

Solving equation 19 for p gives:

$$p = s + t - c$$

Substituting these results in equation 20 gives:

$$y + t + q = p + q/2 - c \text{ or}$$

$$y + t = p - q/2 - c \tag{22}$$

Equations 19, 21, and 22 are, of course, the famous *styx* rules for predicting boron hydride topologies (13).

A similar breakdown may be obtained for any class of compounds which can be represented by a general formula and which contain only certain kinds of bonding components. The neutral hydrocarbons, for example, have the general formula C_mH_n and contain only 2c-2e components. If we let a = number of 2c-2e C-H components and b = number of 2c-2e C-C components, then substitution into equations 6 and 7 gives:

$$U_2 = (4m + n) - (4m + n) = 0$$

$$B_2 = a + b = (4m + n) - (4m + n)/2$$

$$a + b = 2m + n/2$$

Unlike the result with the boron hydrides, the results in these equations are sufficiently trivial so that chemists have always derived topological formulas for the hydrocarbons without having to refer to explicit equations of balance.

The cyclomatic number may also be applied to boron hydride topologies. From the standpoint of graph theory a 3c-2e bond, because it joins three atoms, acts like two edges. Thus substitution in equation 10 gives:

$$\mu = B_2 + 2T_2 - (N + n) + 1$$

Using the definitions of B_2 and T_2 given in equations 17 and 18 gives:

$$\mu = (3E/2 - O) + 2(O - E) - (N + n) + 1$$

$$\mu = O - E/2 - (N + n) + 1$$

$$\mu = (4N + n) - E/2 - (N + n) + 1$$

$$\mu = 3N + 1 - E/2$$

which is the same result as we obtained in equation 11 for electron-precise compounds Using the general formula, $[B_pH_{p+q+c}]^c$ and substituting gives:

$$\mu = 3p + 1 - (3p + p + q)/2 \text{ or}$$

$$\mu = p - q/2 + 1$$

for the number of independent cycles in an acceptable boron hydride VB topology (12). This result may be checked with the examples in figure 5 or those in reference 13.

The successful treatment of boron hydride topologies largely rests on the validity of equation 17, which sets a limit on the number of multicentered components used and thus gives a set of equations of balance capable of unique solution for a given set of E and O values. The idea that a stable species will always prefer additional 2c-2e components when possible rather than a combination of lc-2e and 3c-2e components (a condition which lowers the number of bonding electrons) is one which appeals to chemical instinct (4). Unhappily, it is not a generally valid rule and this is why the *styx* rules do not in general work for other classes of electron-deficient species.

There are many species which, though neither electron rich nor electron deficient, employ both multicentered components and lc-2e components in preference to an increased number of 2c-2e components. B_4Cl_4, for example, gives the result $U_2 = 8$ and $B_2 = 12$ with equations 6 and 7 – a perfectly valid VB topology.
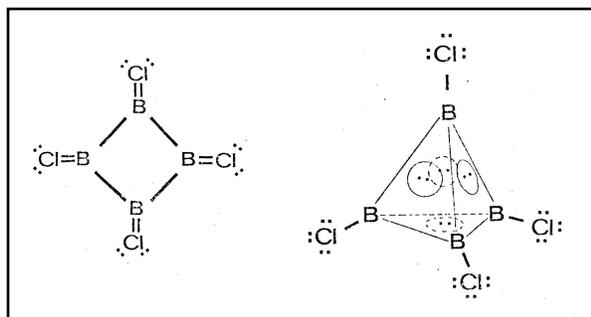
Figure 6a (left): B_4Cl_4, with $B_2 = 12$, $U_2 = 8$, $T_2 = 0$, $\mu = 5$
Figure 6b (right): B_4Cl_4 with $B_2 = 4$, $U_2 = 12$, $T_2 = 4$, $\mu = 5$

The result is shown in figure 6a. The actual topology, however, corresponds to figure 6b. It employs four 3c-2e components and equations 15 and 16 give the values $B_2 = 4$, $U_2 = 12$. The molecule appears to contain an electron-rich portion (i.e., lone pairs) and an electron-deficient portion side by side. The reason the topology in figure 6b is preferred, despite the loss in bonding electrons, is to be found in the auxiliary rules discussed in the final section.

6. Orbital-Rich Species

Unlike the infinite complexes characteristic of nonmolecular solids, stable discrete species cannot have any "dangling" bonds at their periphery; that is, the condition that we are dealing with closed-shell species without empty valence orbitals is equivalent to the requirement that all of the loose ends, so to speak, must be capped either with lone pairs or hydrogen atoms. On the other hand, the orthogonality of the s- and p-orbitals restricts the number of 2c-2e components which may be held in common by any two atoms to no more than three, that is, we do not encounter quadruple bonds in these species. Given these restrictions, the number of lone pairs and terminal hydrogens in a stable discrete species must be such that:

$$U_2 + n \geq 2 \text{ (when N is even)} \qquad (23)$$

$$U_2 + n \geq 4 \text{ (when N is odd)} \qquad (24)$$

Substitution of equation 6 into equations 23 and 24 gives:

$$E \geq 4N + 2 \text{ (when N is even)} \qquad (25)$$

$$E \geq 4N + 4 \text{ (when N is odd)} \qquad (26)$$

Examples of species which fail to meet the conditions set by these equations are the diatomics $NaCl(g)$,

$BeO(g)$, and $C_2(g)$. For all three $E = O = 8$ and equations 6 and 7 yield the results $U_2 = 0$, $B_2 = 4$ or the general formula:

$$A \equiv B$$

This, of course, violates the orthogonality condition and B_2 must be reduced by invoking lc-0e, lc-le, 2c-0e, or 2c-le components, as in equation 14. These species must, therefore, violate either the closed-shell condition or the condition that there be no empty valence orbitals. Consequently they are usually short-lived under ambient conditions and tend to polymerize into infinite three-dimensional complexes.

The problem is not that there aren't enough valence electrons to provide complete VB connectivity using 2c-2e bonds, but rather that there are not enough to do both this and to populate all of the empty valence orbitals as well. Thus these species are also electron-deficient, but in a sense slightly different from those discussed in the last section. For this reason we have used the term *orbital-rich* to distinguish them from species which meet the requirements set by equations 25 and 26 but for which $E < O$.

7. Nonmolecular Solids

When one attempts to extend the VB topology rules given by equations 6 and 7 to the solid state problems result because not all solids are composed of discrete molecules. Indeed, the vast majority of inorganic solids are instead composed of infinite one-dimensional (i.e., chain), two-dimensional (i.e., layer), or three-dimensional (i.e., framework) complexes. If, in the case of such infinite complexes, we define E and O as the total numbers of valence electrons and orbitals respectively per unit formula, equation 6 still gives us the number of lone-pairs per unit formula, but the value of B_2 given by equation 7 will require reinterpretation as the bonding electrons are now not necessarily used to form B_2 2c-2e bonds within the unit formula itself but may be employed in forming 2c-2e bonds between the unit and its neighbors. For solids containing discrete molecules or ions both equations may, of course, be used unaltered.

In approaching this problem we will deal with the structures of the elements first as this simplifies the problem by giving only one kind of atom per unit formula. It is easiest to discuss the bonding topology in these solids in terms of the quantity b/N, where b is the total number of valence electrons available per unit formula for the formation of 2c-2e bonds (i.e., $b = 2B_2$) and N is again the number of heavy s- and p-block atoms per unit formula (i.e., it is assumed no H atoms are present). In other words, b/N is the number of

available bonding electrons per atom. If it is assumed that every 2c-2e bond is formed by each of the two interacting atoms providing an electron, then b/N gives both the total number of 2c-2e bonds per atom and the total maximum possible coordination number (CN) per atom. The actual CN may be less if multiple bonds are formed but b/N will still give the total number of 2c-2e bonds per atom.

Substitution of these definitions into equation 7 and rearrangement gives:

$$b/2 = 4N - E/2 \text{ or}$$

$$b/N = 8 - E/N \qquad (27)$$

The quantity E/N corresponds to the total number of valence electrons per atom, which, in the case of the elements, is the same as their group number G in the periodic table. Thus equation 27 becomes:

$$b/N = 8 - G \qquad (28)$$

This relation was first derived by Hume-Rothery (15) in 1930 and states that the number of bonds formed by an element when in the form of the corresponding simple substance is equal to 8 minus its group number. This

Table 1. Example simple substances illustrating the application of the 8-G rule in equation 28.

U_2	8-G	Element	CN	Structure
0	4	C, Si, Ge, αSn	4/4	framework
0	4	graphite	3/3	planar layers (conjugaed bonds)
1	3	white P	3/3	discrete tetrahedra
1	3	black P, As, Sb	3/3	puckered layers
2	3	N_2	1/1	discrete pairs (triple bond)
2	2	S, Se, Te	2/2	puckered rings & chains
4	2	O_2	1/1	discrete pairs (double bond)
6	1	F_2, Cl_2, Br_2, I_2	1/1	discrete pairs (single bond)
4	0	Ne, Ar, Xe, Rn	0/0	isolated atoms

relation is generally valid only for elements lying to the right of the Zintl line in the periodic table (i.e., groups 4-8). Thus the elements in group 8 are isolated atoms since $b/N = 0$ and $U_2 = 4$ by equation 6. Elements in group 7 give $b/N = 1$ and $U_2 = 6$; elements in group 6, give $b/N = 2$ and $U_2 = 2$, etc. Further examples are displayed in Table 1.

Pearson (16) has shown that equations similar to 6 and 27 may also be used to rationalize the VB topology of the anion-anion bonding in most semiconductors, insulators, and ionic compounds whose anionic (i.e., electronegative) components likewise lie to the right of the Zintl line. A binary solid of the general formula C_cA_a, for instance, is treated as though its C-A bond is completely ionic, that is, as if it contains only homonuclear cation-cation bonds, homonuclear 2c-2e anion-anion bonds, but no polar covalent cation-anion bonds, these components being held together instead by their net ionic charges. Equations 6 and 27 are then applied to the anionic components only:

$$U_{2a} = E - b_c - 4N_a \qquad (29)$$

$$b_a/N_a = 8 - (E - b_c)/N_a \text{ or}$$

$$8 = (E + b_a - b_c)/N_a \qquad (30)$$

where N_a is the total number of anionic atoms per unit formula and b_c is the total number of electrons per unit formula involved in cation-cation bonding or in cation lone pairs. $E - b_c$ is, therefore, the total number of anionic electrons per unit formula, U_{2a} is the total number of anionic lone pairs per unit formula, b_a is the total number of electrons involved in 2c-2e anion-anion bonds per unit formula, and b_a/N_a is the number of electrons per anion available for 2c-2e anion-anion bonding. Equation 30 is known as the generalized 8-N or 8-G rule and is the subject of an extensive literature (16-20).

Applying equations 29 and 30 to $[NaCl]_{3D}$ (21) ($b_c = 0$, $N_a = 1$, $E = 8$) gives $U_{2a} = 4$ and $b_a/N_a = 0$, corresponding to isolated Cl$^-$ ions. Likewise, applying the equations to $[CaSi_2]_{2D}$ ($b_c = 0$, $N_a = 2$, $E = 10$) gives $U_{2a} = 2$, and $b_a/N_a = 3$. The actual topology for the Si$^-$ anion is that of an infinite two-dimensional hexagonal net, each Si atom having $CN = 3$. Since there is one lone-pair per Si atom, the actual net is puckered. In short, the anionic bonding topology and geometry are generally isomorphous with that of the corresponding isoelectronic neutral element (in the above examples Ar and As). Further examples are given in Table 2 or may be obtained by consulting the reviews by Pearson (16) and by Schafer *et al* (22).

The reason that equations 28, 29 and 30 are restricted to species lying to the right of the Zintl line is that they are all essentially versions of equations 6 and 7 and must therefore meet the conditions under which 6 and 7 are valid. The requirement that the constituent atoms come from groups 4-8 insures that $E \geq O$ and that we are not dealing with electron-deficient bonding. Such species are called valence compounds and Pearson has used equation 30 to classify them as *normal* valence compounds (for which $b_a/N_a = 8$ or one has isolated cations and anions), *polyanionic* valence compounds (for which $b_a/N_a < 8$ and one must have anion-anion bonding), and *polycationic* valence compounds (for which $b_a/N_a > 8$ and one must have cation-cation bonding).

Table 2. Example binary compounds illustrating the application of the generalized *8-G* rule equation 30.

U_{2a}	b_a/N_a	Compounds	CN_a	Anionic Structure
0	4	LiAl, NaIn, SrIn$_2$, BaTl$_2$	4/4	framework
1	3	NaSi, KeGe RbP, CsSn	3/3	discrete tetrahedra
2	3	CaSi$_2$	3/3	puckered layers
2	3	CaC$_2$	1/1	discrete pairs (triple bond)
2	2	LiP, NaSb, LiAs, KSb	2/2	puckered chains
3	1	CaP	1/1	discrete pairs (single bond)
4	0	KF, NaCl, CsBr	0/0	isolated mono-atomic anions

Precisely why the ionic formalism works as well as it does for these compounds is not completely understood (20). However, the number of lone pairs assigned to the anionic components by equation 29, while usually giving proper geometry predictions using the VSEPR rules, is probably only formal. These electrons may actually be involved in cation-anion bonds of varying degrees of ionicity. Because there is no Zintl line requirement for the cationic components this cation-anion bonding may or may not be electron deficient.

8. Auxiliary Rules: Connectivity Constraints

All of the above electron and orbital counting rules have set constraints on the numbers and kinds of bonding components which are consistent with a given total number of valence electrons and valence orbitals. In this section we deal with rules which restrict the manner in which these components may be assembled to give plausible bonding topologies. All of these rules were implicitly assumed in constructing the example topologies in the various figures and at least one – the orthogonality restraint controlling the number of 2c-2e components shared in common by any two atoms – was explicitly discussed above.

The most familiar rule in this class is the octet rule. It states that the total number of electrons per atom, summed over all the components belonging to it, must be eight (or two for hydrogen). It therefore sets a limit on the total connectivity of each atom. The rule is apparently always valid for long-lived species composed of period 2 elements. However, a debate has been in progress for some time now as to whether or not s- and p-block elements from period 3 on can violate the rule by using outer d orbitals (23). In the case of the electron-rich species discussed above this would alter the value of O, and hence the conditions set by equation 12, and allow a satisfactory representation of these species with a single VB topology using only 2c-2e and lc-2e components. Theoretical studies, however, have for the most part ruled against this possibility and have favored instead the use of multicentered bonding components and the general maintenance of the octet rule for all of the s- and p-block elements (24, 25).

The effective atomic number rule or *EAN* rule is often used to set connectivity limits for the transition metals. However, it is not of the same fundamental nature as the octet rule. In the case of octahedral complexes at least, Mitchell and Parish have shown that its validity is highly dependent on the nature of the ligands involved (26). Ligands which cannot participate in back-donation and which give weak ligand fields leave both the t$_{2g}$ and e$_g$* MO's nonbonding or weakly antibonding. Their occupation, therefore, tends to be energetically undecisive and such complexes may contain from 12 to 22 valence electrons about the central atom. Those ligands which cannot participate in back-donation but which give strong ligand fields make the e$_g$* orbitals decidely antibonding, but still leave the t$_{2g}$ orbitals nonbonding. Their occupation is again energetically undecisive and such complexes may contain from 12 to 18 electrons about the central atom. Finally, those ligands which both participate in back-donation and give strong ligand fields not only

make the e_g^* orbitals strongly antibonding but the t_{2g} orbitals decidedly bonding in nature. These complexes always contain 18 electrons and obey the so-called *EAN* rule.

The second important topological restraint is the electroneutrality principle. This was first stated by Langmuir in 1921 in terms of formal charge distributions (27). The rule was later refined by Pauling, who allowed for differences in electronegativity or bond ionicity (28-30). In terms of formal charge distributions it requires that the net formal charge on each atom in an acceptable topology be approximately between the limits of 1+ and 1- and that the signs of the charges be consistent with the relative electronegativities of the atoms. If the factor of bond ionicity is taken into account, these limits are smaller, lying between 0.5+ and 0.5- in Pauling's treatment, for example.

Thus, while both of the B_4Cl_4 topologies in figures 6a and 6b obey the octet rule, that in figure 6b gives a formal charge of zero for all of the atoms, whereas that in figure 6a places a 1+ charge on each Cl and a 1- charge on each B. These are within acceptable limits but distribute the charges in a manner at variance with the relative electronegativities of boron and chlorine. Hence the topology in figure 6b is preferred despite the apparent loss in effective bonding electrons. The use of multicentered bonding components generally gives better formal charge distributions. Although usually neglected in the freshman text, the electroneutrality principle is at least as important as the octet rule in determining bonding topology.

9. Summary and Conclusions

A set of general equations (4 and 5) for determining the numbers and kinds of bonding components consistent with a given set of total valence electron and orbital values was derived within the context of the hybrid MO description. By placing special constraints on these equations (no multicentered bonds, use of "no-bond" resonance structures, expanded octets, the ionic formalism, use of 3c-2e components coupled to the condition that $U_2 = 0$, etc.) special topological equations of balance were derived for conventional VB - Lewis dot structures, for electron-rich species, electron-deficient species, and orbital-rich species. The *styx* rules and the conventional and generalized *8-G* rules were also derived as special cases of equations 4 and 5. In short, all of the qualitative topology rules found in our textbooks are special cases of a general orbital-electron counting procedure and are obtained by invoking special auxiliary conditions which are reasonably valid for certain classes of compounds.

The orbital picture of molecules and atoms is, of course, an approximation in itself and it is apparent that our qualitative rules for predicting topologies are less general and less reliable than our rules for predicting molecular geometry. We have, for instance, carefully avoided mention of species containing the transition elements because of the ambiguities involved in counting up their effective valence electrons and orbitals. Nevertheless, such topology rules still form an important part of the general chemistry curriculum.

10. References and Notes

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