

Topological Atomic Charges, Valencies, and Bond Orders<sup>†</sup>

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Theorems and corollaries are proved and relationships are derived for the atomic and bond moments of energy in molecules and solids or, in terms of graph theory, for the self-returning walks *SRWs* that begin in graph vertexes and edges, respectively. Topological atomic charges, valencies, and bond orders are introduced by means of the limit distributions of the *SRWs*. A hierarchical system of topological rules on atomic and bond reactivity is presented proceeding from the alternating positive and negative contributions to the atomic and bond moments. Some light is thus shed on the topological control of chemical reactivity.

## INTRODUCTION

The contemporary understanding of chemical reactivity<sup>1,2</sup> arose from the Hückel molecular orbital theory which is based on molecular topology (nearest neighbor or *adjacency* relationships in molecules). The concepts of atomic charges, free valencies, and bond orders, based on molecular orbital coefficients, proved to be fruitful, particularly after recognizing the importance of frontier orbitals.<sup>3</sup> However, with the progress in semiempirical and *ab initio* molecular orbital methods, the emphasis was shifted to obtaining numerical data rather than to further studies on the topological routes of chemical reactivity.

Within the valence bond quantum chemical theory a different bond order concept was proposed by Pauling.<sup>4</sup> He defined the  $\pi$ -bond order in a conjugated molecule as the relative frequency of occurrence of a certain double bond in all Kekulé structures describing the molecule. Once again, this definition is topological in nature since the Kekulé structures correspond to *perfect matchings* of molecular graph (the set of disjoint edges which cover all vertexes). However, until very recently this concept was subjected to no further development.

The last 25 years marked an ever increasing process of topologization of chemistry, as a result of the efforts of many researchers in the field of chemical graph theory.<sup>5–14</sup> Numerous molecular topology descriptors<sup>15–20</sup> were developed and applied in the modeling of properties of chemical compounds, in drug design, in assessing environmental toxicities, and in other areas. Most of these topological indexes or graph-invariants characterize the entire molecule or its fragments. The *atomic* and *bond* indexes introduced were regarded mainly as contributing to the global molecular properties rather than dealing with the major property of atoms and bonds in molecule, their reactivity.<sup>21,22</sup> The atomic connectivity indexes of Kier and Hall<sup>23</sup> were found to correlate highly with the *CNDO/2* atomic charges in alkanes.<sup>24,25</sup> The charge indexes of Gálvez et al.<sup>26</sup> (which are actually atomic charge transfer indexes) were found to

correlate satisfactorily with molecular dipole moments but were not compared to the atomic charges. Randić and Guo<sup>27</sup> modified the Pauling bond order by using weighted Kekulé structures within the conjugated circuits model.<sup>28</sup> Randić and co-workers<sup>29</sup> specified a *graphical bond order* to each bond as a ratio of the values of selected invariant of the subgraph *G-e* and graph *G*, the former being obtained from *G* by deleting edge *e*. Several best known topological indexes have been used to illustrate the idea. However, applicable to cyclic molecules only, the graphical bond orders thus defined has been used as bond-additive quantities to characterize the global molecular properties but not bond reactivity.

Self-returning walks *SRWs* in graphs (walks that start and end at the same graph vertex) were used by Jiang and Zhang<sup>30</sup> to define point-energy and edge-energy as measures for site and bond reactivity, respectively. Bonchev, Kier, and Mekenyan<sup>31</sup> proposed topological atomic charges and valencies proceeding from the limit distribution of atomic self-returning walks and its second moment scaling. The basis of this approach is the recently proved<sup>32</sup> finding that the limit for the relative atomic self-returning walks equals the respective squared principal eigenvector coefficients, i.e., they are partial atomic charges corresponding to the lowest occupied molecular orbital (LOMO). In this paper we develop further these ideas by introducing the concept for a *SRW*-based topological bond order, by devising relationships for the topological atomic and bond descriptors as well as by devising topological rules on chemical reactivity.

## THE BACKGROUND

Self-returning walks (*SRWs*) in molecular graphs have long been of interest for theoreticians, e.g., for the characterization of atomic environments in molecules,<sup>33</sup> the graph center,<sup>34</sup> and isocodal and isospectral vertexes and edges.<sup>35–37</sup> However, the interest toward this graph-invariant has drastically increased during the last 10 years, after recognizing that it is *SRWs* that control topologically stability and other properties of molecules via the method of moments of energy.<sup>38–43</sup> Formulas have been derived for the *SRWs* of several classes of graphs and graph vertexes;<sup>44</sup> molecular branching patterns were interpreted and generalized on this basis.<sup>44,45</sup>

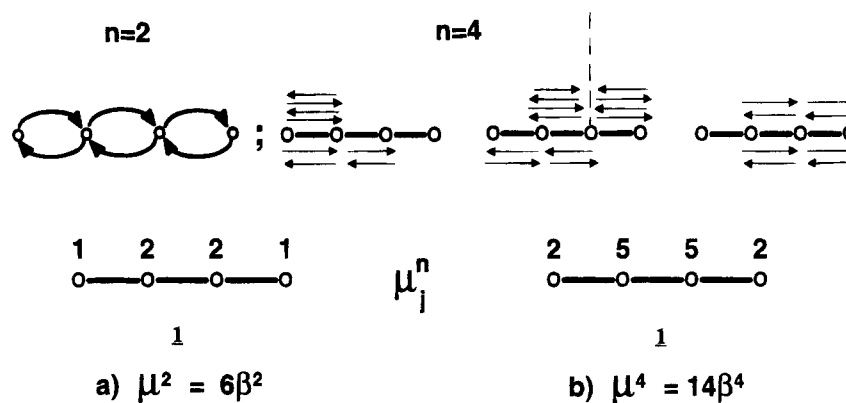
Let a molecule be described by a spectrum of eigenvalues  $E_1, E_2, \dots, E_j, \dots, E_n$ , associated with an orthonormal basis

<sup>†</sup> Dedicated to A. T. Balaban, the pioneer of chemical graph theory, for his numerous contributions and for the long years of friendship and cooperation.

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**Figure 1.** Six self-returning walks of length two and 14 walks of length four in the hydrogen depleted molecular graph of butadiene. *SRWs* are shown for one terminal and one central atom (solid circles) only.

$c_1, c_2, \dots, c_j, \dots, c_n$ , of corresponding eigenvectors with  $c_{ji}$  being the  $i$ th coefficient of  $c_j$ . The molecular  $k$ th moment of energy,  $\mu^k$ , is defined as the sum of all  $k$ th power eigenvalues. Due to the invariance of the trace of the corresponding Hamiltonian matrix upon the diagonalization used in solving the secular system of equations, one obtains

$$\mu^k = \sum_i E_i^k = \text{Tr}(H^k) \quad (1)$$

The trace of the  $k$ th power Hamiltonian has a simple topological interpretation. It equals the weighted sum of all *SRWs* of length  $k$  in the molecule, that begin and end with the same orbital

$$\mu^k = \sum_i \sum_j H_{ij} H_{jm} \dots H_{si} \quad (2)$$

The term is the product of " $k$ " elements of the Hamiltonian matrix. The weights associated with the walk are the interaction integrals  $H_{jab}$  involving the overlapping orbitals  $ja$  and  $jb$ . The simplest weighing results from the Hückel-type model in which all  $H_{jab} = \beta$ , if  $ja$  and  $jb$  are  $p_\pi$  orbitals located on atoms of a  $\pi$ -bonded network. In this case, the  $k$ th moment of the  $i$ th orbital,  $\mu_i^k$ , is determined by the number of walks  $SRW_i^k$  that start at this orbital and return to it in  $k$  steps, traversing one bond in each step:

$$\mu_i^k = SRW_i^k \beta^k \quad (3)$$

Correspondingly, the  $k$ th molecular moment is calculated from the total number of *SRWs* in the molecule:

$$\mu^k = \sum_i \mu_i^k = SRW^k \beta^k \quad (4)$$

An illustration is presented in Figure 1 where the second and fourth moments of the butadiene molecule are expressed by the respective *SRWs* of length two and four.

#### RELATIVE ATOMIC MOMENTS AS TOPOLOGICAL ATOMIC CHARGES

The moments of energy are very sensitive to the major topological features of molecules, namely their branching, cyclicity, and centrality.<sup>31,32,34,44,45</sup> However, their number increases rapidly with the walk length  $k$ . A natural way of avoiding the difficulties in dealing with very large numbers was to introduce<sup>31</sup> the *relative atomic moments (RAMs)*,  $f_i^k$

$$f_i^k = \mu_i^k / \mu^k = SRW_i^k / \sum_i SRW_i^k = SRW_i^k / SRW^k \quad (5)$$

It was easy to find that *RAMs* always have a limit. However, it was a surprise to find (by calculations of up to the 100th moments) that this limit equals the respective squared atomic coefficient in the principal eigenvector  $c_{ii}^2$ . This finding<sup>31</sup> was later proved rigorously.<sup>32</sup>

$$f_i = \lim_{k \gg 1} f_i^k = \lim_{k \gg 1} \mu_i^k / \mu^k = \lim_{k \gg 1} (SRW_i^k / SRW^k) = c_{ii}^2 \quad (6)$$

Thus, the relative atomic moments of energy  $f_i$  appear as partial atomic charges; they express the one-electron charge distribution on atoms produced by the principal eigenvector. This interpretation resulted in the following conjecture.<sup>31</sup>

**Each atomic self-returning walk in molecular graph is in a certain way associated with electron motion near the nucleus of this atom.**

The relative atomic moment  $f_i$  was thus interpreted as relative frequency of electron motion near atom  $i$ .

These results, obtained in 1990 and published<sup>31</sup> only in 1993, were reminiscent of the Feynman path integral method which accounts for **all** electron paths.<sup>46</sup> The anticipated close analogy was soon confirmed. In 1992, Nagao, Nishikawa, and Aono<sup>47</sup> applied the path integral method to the Hückel model and, in summing contributions of all independent electron trajectories, derived formulas which numerically reproduced the known results for the number of *SRWs* in linear and monocyclic molecular graphs. In this way, the quantum mechanical background of the self-returning walks, known through the method of moments, was confirmed independently by the Feynman path integral method. We thus arrive at a new *SRW* interpretation.

**Each self-returning walk in molecular graph corresponds to an independent Feynman's electron trajectory.**

The same interpretation may be made for the open walks (those that begin and end in different atoms) which also constitute path integral contributions. We may thus generalize that *molecular graphs encode information on all electron trajectories in the molecule*. This could be the key to the understanding of why molecular graphs describe so well molecular properties.

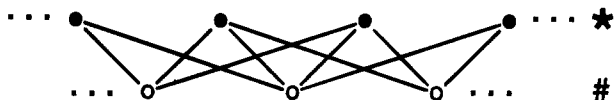
#### A THEOREM FOR ATOMIC MOMENTS IN ALTERNANT MOLECULES AND SOLIDS

Alternant molecules and solids are composed of two subsets of atoms, starred (\*) and unstarred (#), with the property that two atoms of the same subset are never adjacent. Molecular graphs of these systems are *bipartite*

graphs. Their vertexes are partitioned into starred  $\{V^*\}$  and unstarred ( $V^\#$ ) subsets. The following holds.

**Theorem:** In alternant molecules and solids the sum of the  $k$ th atomic moments of all starred atoms is equal to that of all unstarred atoms for any  $k$ .

$$\sum_{i^*} \mu_i^k = \sum_{j^\#} \mu_j^k \quad (7)$$



Proof: Each edge  $\{ij\}$  in a bipartite graph is formed by two vertices:  $i \in \{V^*\}$  and  $j \in \{V^\#\}$ . Each edge  $\{ij\}$  can also be represented by two arcs emanating from  $i$  and  $j$ , respectively, i.e., it is a self-returning walk of length 2 for both  $i$  and  $j$ . Therefore, each edge contributes equally to the sums of second moments of starred and unstarred atoms. Each walk of length  $k$ , starting in  $i$  and  $j$ ,  $SRW_i^k$  and  $SRW_j^k$ , is composed of  $k$  edges; hence, taking into account eq 3, the contributions to the two sums of moments are always equal.

**Corollary 1:** In alternant molecules and solids the sum of the  $k$ th relative atomic moments of the starred atoms is equal to that of the unstarred atoms for any  $k$ .

$$\sum_{i^*} f_i^k = \sum_{j^\#} f_j^k \quad (8)$$

The proof follows directly from eq 7 on dividing it by the  $k$ th total moment  $\mu^k$  of the molecule or solid. The corollary covers the limit distribution  $f_i^s$  of the relative atomic moments for  $k \gg 1$ . Since  $f_i^s$  were shown to be one-electron atomic charges, corollary 1 can be interpreted as equality of the one-electron topological charge of all starred and all unstarred atoms

$$\sum_{i^*} f_i = \sum_{j^\#} f_j = 1/2 \quad (8a)$$

Figure 2 illustrates the theorem with one acyclic and one cyclic molecule.

In the next sections we make use of eqs 8 and 8a to derive relationships for the relative atomic moments and topological bond orders.

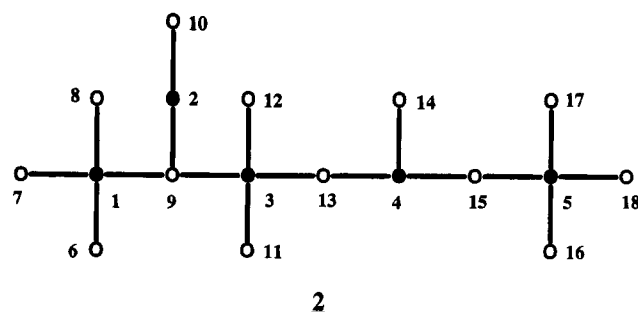
**Corollary 2:** In alternant molecules and solids each  $k$ th (absolute and relative) atomic moment, including the limit for  $k \gg 1$ , is formed by positive contributions from all odd-numbered neighboring atoms and negative contributions from all even-numbered neighboring atoms

$$\mu_i^k = \sum_{j(i)} \mu_j^k - \sum_{s(j)} \mu_s^k + \sum_{t(s)} \mu_t^k - \sum_{u(t)} \mu_u^k + \dots \quad (9)$$

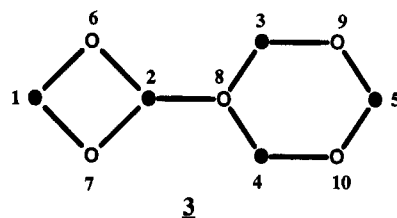
$$f_i = \sum_{j(i)} f_j - \sum_{s(j)} f_s + \sum_{t(s)} f_t - \sum_{u(t)} f_u + \dots \quad (9a)$$

where the abbreviation  $x(y)$  is used for all vertexes  $y$  adjacent to  $x$ . The proof follows directly from eqs 8 and 8a after solving them with respect to a particular  $\mu_i^k$  and  $f_i$ , respectively.

The alternating contributions to  $\mu_i^k$  and  $f_i$  are illustrated in Figure 3 for an arbitrary chosen atom assigned as zero-vertex.

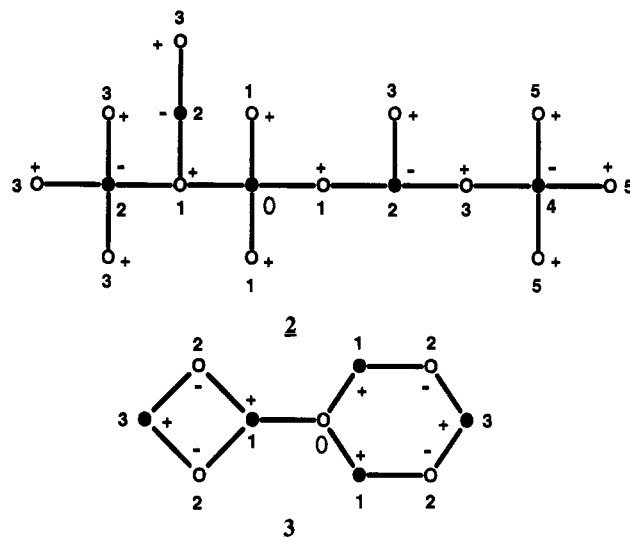


$$\sum_{i^*=1}^5 \mu_i^k = \sum_{j^\#=6}^{18} \mu_j^k ; \quad \sum_{i^*=1}^5 f_i^k = \sum_{j^\#=6}^{18} f_j^k$$



$$\sum_{i^*=1}^5 \mu_i^k = \sum_{j^\#=6}^{10} \mu_j^k ; \quad \sum_{i^*=1}^5 f_i^k = \sum_{j^\#=6}^{10} f_j^k$$

**Figure 2.** Two alternant molecules illustrating the theorem on atomic moments and its corollary. The two subsets of vertexes are presented by solid and open circles, respectively.



**Figure 3.** Illustration of the alternating contributions to the absolute and relative moments of an arbitrarily chosen atom denoted by zero, whereas its first, second, etc. neighbors are denoted by 1, 2, etc.  $\mu_0^k = \sum \mu_1^k - \sum \mu_2^k + \sum \mu_3^k - \sum \mu_4^k + \sum \mu_5^k$ .

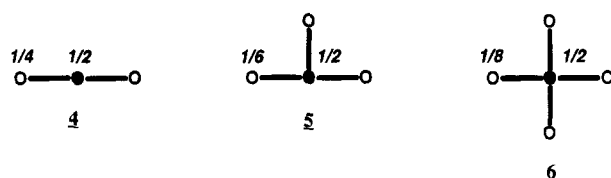
It will be shown later that (9) and (9a) are specific cases of a more general formula comprising also nonalternant structures.

#### ATOMIC MOMENT DISTRIBUTIONS IN SOME CLASSES OF ACYCLIC MOLECULES

Denote the number of graph vertexes by  $n$  and the number of branches in an acyclic graph by  $b$ . The following

relationships hold for the limit distribution of relative atomic moments.

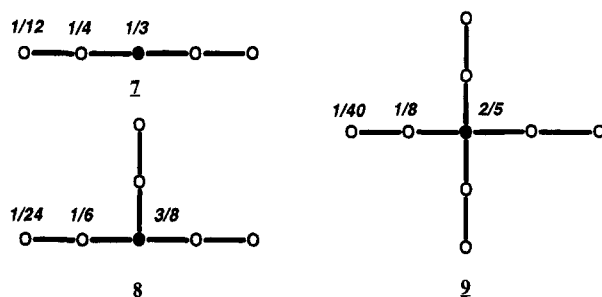
### Star-graphs



$$f_{\text{terminal}} = 1/[2(n-1)] = 1/2b \quad (10)$$

$$f_{\text{central}} = 1/2 = bf_{\text{terminal}} \quad (11)$$

### Star-like graphs



$$f_{\text{terminal}} = 1/[2b(b+1)] \quad (12)$$

$$f_{\text{middle}} = 1/(2b) \quad (13)$$

$$f_{\text{central}} = b/[2(b+1)] = b^2 f_{\text{terminal}} \quad (14)$$

### Dendrites

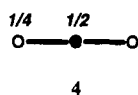
Let the number of new branches at each vertex is denoted by  $b$ , and the number of generations be denoted by  $g$ . For  $g = 1$  or  $2$

$$f_{\text{central}} = (1/2)^g \quad (15)$$

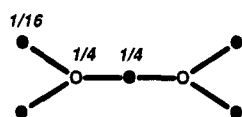
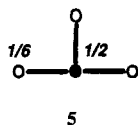
$$f_{\text{terminal}} = (1/2b)^g \quad (16)$$

$$f_{\text{central}}/f_{\text{terminal}} = b^g \quad (17)$$

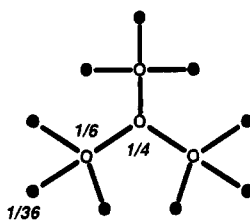
#### 2-dendrites



#### 3-dendrites

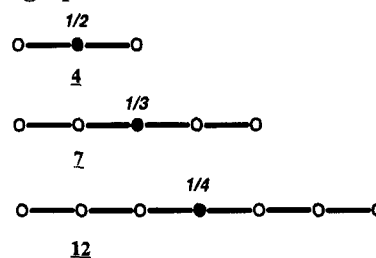


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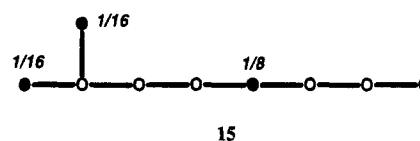
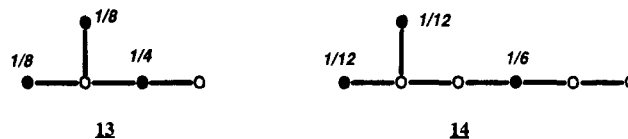
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### Odd path graphs



$$f_{\text{central}} = 2/(n+1) \quad (18)$$

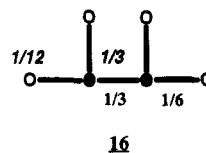
**Snake graphs** (Tree graphs having a single branch at position 2)



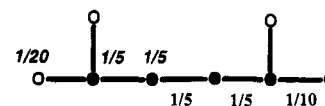
$$f_{\text{terminal}} = 1/[2(n-1)] \quad (19)$$

$$f_{\text{central(main branch)}} = 1/(n-1) = 2f_{\text{terminal}} \quad (20)$$

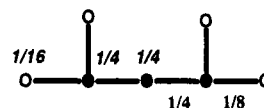
**Double snake graphs** (Tree graphs having a single branch at position 2 and another single branch at position  $\omega - 1$ )



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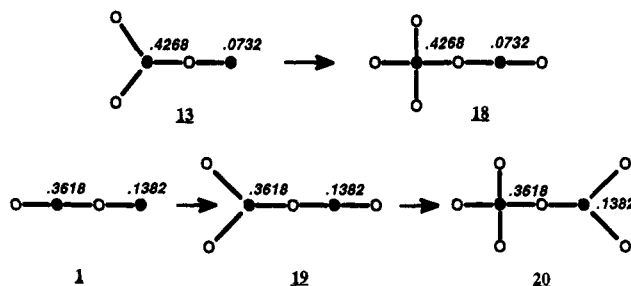
$$f_{\text{nonterminal}} = 1/(n-3) = \text{const} \quad (21)$$

$$f_{\text{terminal}} = 1/[4(n-3)] \quad (22)$$

**Transformations preserving RAMs.** Several interesting cases were found in which a pair of second-neighbor atoms  $i$  and  $j$  have their relative atomic moments invariant to some special additive transformations (Figure 4 as well as the dendrite structures). The latter include a successive simultaneous addition of atoms to  $i$  and  $j$ , so that the respective vertex degrees  $a_i$  and  $a_j$  simultaneously increase by one:  $a_i = 1 \rightarrow 2 \rightarrow 3$ ;  $a_j = 2 \rightarrow 3 \rightarrow 4$  (Figure 4) or by two or three:  $a_i = a_j = 1 \rightarrow 3$  or  $1 \rightarrow 4$  (dendrite vertexes adjacent to the graph center).

### TOPOLOGICAL BOND ORDERS (ONE-ELECTRON CHARGE DISTRIBUTION OVER BONDS)

In the foregoing we have shown that the limit distribution for the ratio of the number of self-returning walks that begin



**Figure 4.** Two cases of preserving the relative atomic moments (the topological charges) of a pair of atoms (solid circles) upon successive addition of atoms.

and end in an atom and the total number of such walks expresses the one-electron charge distribution over atoms associated with the principal eigenvector. We called these charges topological atomic charges. Analogously, we define here **topological bond orders**  $p_{ij}(A)$  as limit distribution for the ratio of the number of self-returning walks beginning and ending in the edge  $ij$ , and the total number of SRWs of the same length.

$$p_{ij}^k(A) = (SRW_{ij}^k + SRW_{ji}^k) / SRW^k \quad (23)$$

$$p_{ij}(A) = \lim_{k \gg 1} p_{ij}^k(A) = \lim_{k \gg 1} ((SRW_{ij}^k + SRW_{ji}^k) / SRW^k) \quad (24)$$

An alternative definition for  $p_{ij}(B)$  was proposed proceeding from the analogous limit for the ratio of the total number of edges  $E_{ij}^k$  and  $E_{ji}^k$ , that are traversed by all self-returning walks of the same length  $k$ , and the total number of edges  $E_{total}^k = kSRW^k$  these walks contain:

$$p_{ij}(B) = \lim_{k \gg 1} p_{ij}^k(B) = \lim_{k \gg 1} ((E_{ij}^k + E_{ji}^k) / (kSRW^k)) \quad (25)$$

Definition (25) may be regarded as a further extension of the idea of Pauling's bond order from (i) the occurrence of the double bonds in all Kekulé structures, to (ii) that in all Randić's conjugated circuits, to (iii) the occurrence of a bond in all self-returning walks.

In fact, the two kinds of topological bond orders introduced above are always equal

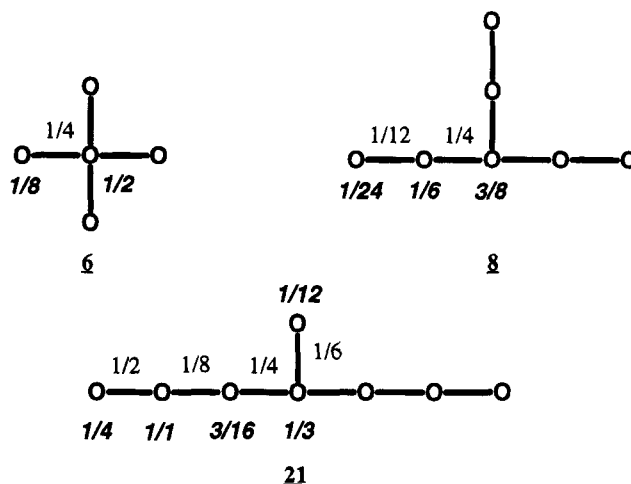
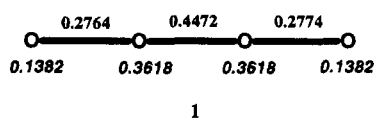
$$p_{ij}(A) = p_{ij}(B) \quad (26)$$

This equality follows from the definition of self-returning walks which requires the number of such walks that start and that end in a vertex to be the same. More detailed analysis is presented related to the proof of Theorem 2.

The topological bond orders thus defined are in fact a one-electron distribution over bonds in a molecule, analogous to the one-electron distribution over atoms which we defined as topological atomic charges

$$\sum_{\text{all atoms}} f_i = \sum_{\text{all bonds}} p_{ij} = 1 \quad (27)$$

Both distributions are illustrated below with the molecular graph of butadiene.



**Figure 5.** Illustration of some cases for which the topological bond order equals the partial LOMO bond order.

However, there is a major difference between the two topological descriptors. While the topological atomic charges equals the atomic charges in the lowest occupied molecular orbital, the topological bond orders are generally different from the respective one-electron LOMO bond orders:

$$p_{ij}(A) = p_{ij}(B) \neq p_{ij}(LOMO) = c_i c_j = (f_i f_j)^{1/2} \quad (28)$$

The few exceptions found, for which inequality (28) turns into equality include the trivial case of the monocyclic structures, as well as the double snake graphs and some other cases shown in Figure 5.

In a few cases  $p_{ij}$  has the same value for a pair of nonequivalent bonds. These are the bonds corresponding to the endspectral edges in graphs. Figure 6 shows such an example in trees having a single branch in position 2 or 3. By denoting the number of atoms in the longest branch by  $n_l$ , the degenerate bond order in these structures is given by the formula

$$p_{ij} = 1/(n_l + 1) \quad (29)$$

#### THEOREMS RELATING TOPOLOGICAL ATOMIC AND BOND MOMENTS (ATOMIC CHARGES AND BOND ORDERS)

**Definition 1:**  $k$ th edge self-returning walk count,  $SRW_{ij}^k = SRW_{ij}^k(1) + SRW_{ji}^k(2)$ , is defined as the count of all SRWs of length  $k$  that start with the edges  $ij$  and  $ji$ , respectively.

**Definition 2:**  $k$ th bond moment  $\mu_{ij}^k = \mu_{ij}^k(1) + \mu_{ji}^k(2)$  is defined as a product of the respective powers for edge self-returning walk count and resonance integral

$$\mu_{ij}^k = SRW_{ij}^k \beta^k \quad (30)$$

**Bond moment**  $\mu_{ij}$  is defined as the limit of  $\mu_{ij}^k$  for  $k \gg 1$ .

**Theorem 2:** Any  $k$ th moment of any atom  $i$  in a molecule or solid is equal to the sum of  $k$ th bond moment components  $\mu_{ji}^k(2)$  of its first neighbors  $j$

$$\mu_i^k = \sum_{j(i)} \mu_{ji}^k(2) \quad (31)$$

**Proof:** The relation between the vertex and edge SRWs is given by the equation

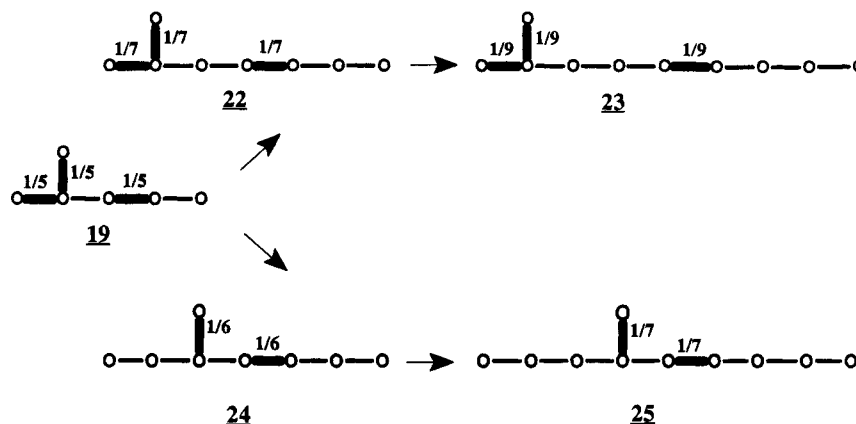


Figure 6. Illustration of the degeneracy of the topological bond order for some nonequivalent bonds (depicted by thick lines).

$$SRW_i^k = \sum_{j(i)} SRW_{ij}^k(1) \quad (32)$$

On the other hand, since all  $SRW$ s are built from  $SRW^2$ s, the definition for a self-returning walk requires the number of such walks that begin in a vertex to be equal to the number of walks that end in it

$$\sum_{j(i)} SRW_{ij}^2(1) = \sum_{j(i)} SRW_{ji}^2(2) \quad (33)$$

Hence, as well as from eq 3 and Definition 2, it follows that

$$\mu_i^k = \sum_{j(i)} \mu_{ij}^k(1) = \sum_{j(i)} \mu_{ji}^k(2) \quad (31a)$$

**Theorem 3:** The sum of the topological bond orders  $p_{ij}$  of all bonds  $ij$  formed by atom  $i$  is equal to the doubled topological atomic charge  $f_i$

$$\sum_{j(i)} p_{ij} = 2f_i \quad (34)$$

Proof: From eqs 24, 33, and 32 one obtains

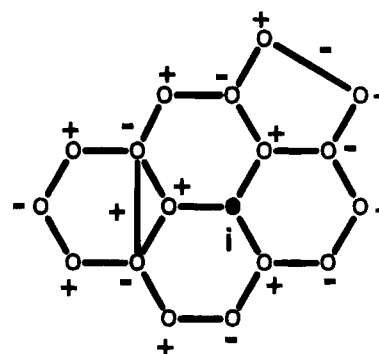
$$\sum_{j(i)} p_{ij} = \lim_{k \gg 1} \sum_{j(i)} p_{ij}^k = \lim_{k \gg 1} ((2 \sum_{j(i)} SRW_{ij}^k(1)) / SRW_i^k) = 2f_i \quad (34a)$$

**Corollary 1:** Each  $k$ th absolute and relative atomic moment in a molecule or solid, including the limit for  $k \gg 1$ , is formed by positive and negative contributions from all odd-numbered and even-numbered neighboring atoms, respectively, as well as from positive and negative contributions of bonds (if they exist) between even,even-numbered and odd,odd-numbered neighboring atoms, respectively.

$$\mu_i^k = \sum_{j[i]} \mu_j^k - \sum_{s[[i]]} \mu_s^k + \sum_{s[[i]]} \mu_{ss}^k - \sum_{j[i]} \mu_{jj}^k \quad (35)$$

$$f_i = \sum_{j[i]} f_j - \sum_{s[[i]]} f_s + \sum_{s[[i]]} p_{ss} - \sum_{j[i]} p_{jj} \quad (35a)$$

Here,  $j[i]$  and  $s[[i]]$  stand for all odd-numbered and all even-numbered neighbors of  $i$ , respectively. Equation 35 is obtained after successive applying of eq 34 to the first, second, etc. neighbors of atom  $i$ . Hence, eq 35a is directly



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obtained after making use of the definitions for  $\mu_i^k$ ,  $f_i$ ,  $p_{ij}$ , and  $\mu_{ij}$  (eqs 3, 6, 23, and 30, respectively).

The bond contributions in eqs 35 and 35a are zero for all alternant molecular or crystal systems; therefore, eqs 9 and 9a can be obtained as specific cases of eqs 35 and 35a, respectively.

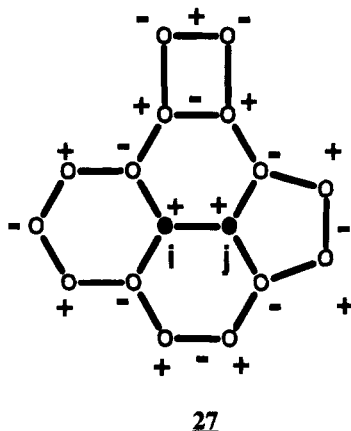
**Corollary 2:** Each  $k$ th absolute and relative moment of the  $ij$  bond in a molecule or solid, including the limit for  $k \gg 1$ , is formed by positive and negative contributions from all even-numbered and odd-numbered neighboring atoms of both  $i$  and  $j$ , respectively, as well as from positive and negative contributions of bonds (if they exist) between odd, odd-numbered and even,even-numbered neighboring atoms, respectively.

**Corollary 2:** Each  $k$ th absolute and relative moment of the  $ij$  bond in a molecule or solid, including the limit for  $k \gg 1$ , is formed by positive and negative contributions from all even-numbered and odd-numbered neighboring atoms of both  $i$  and  $j$ , respectively, as well as from positive and negative contributions of bonds (if they exist) between odd, odd-numbered and even,even-numbered neighboring atoms, respectively.

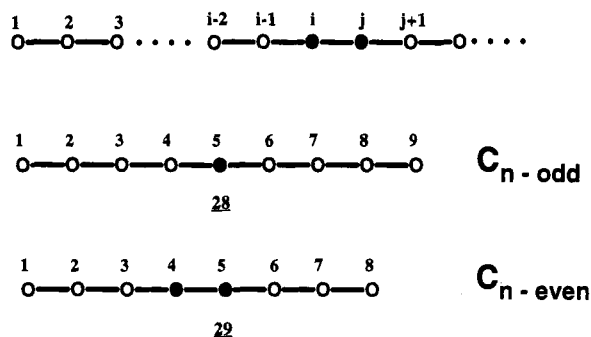
$$p_{ij} = f_i + f_j - (\sum_{h[i]} f_h + \sum_{l[j]} f_l) + (\sum_{g[[i]]} f_g + \sum_{m[[j]]} f_m) - \sum_{gm} p_{gm} + \sum_{hk} p_{hl} \quad (36)$$

$$\mu_{ij}^k = \mu_i^k + \mu_j^k - (\sum_{h[i]} \mu_h^k + \sum_{l[j]} \mu_l^k) + (\sum_{g[[i]]} \mu_g^k + \sum_{m[[j]]} \mu_m^k) - \sum_{gm} \mu_{gm}^k + \sum_{hk} \mu_{hl}^k \quad (36a)$$

Here again, the single and double square brackets are used for odd-numbered and even-numbered neighborhood relationships (they are omitted for brevity in the last two terms



**Figure 8.** Alternating contributions to the moment of energy and to the bond order of bond  $ij$ : positive from atoms  $i$  and  $j$  and their second, fourth, etc. neighbors, negative from their first, third, etc. neighbors, as well as positive contribution from a bond between two third neighbors and negative ones from three bonds between pairs of second neighbors.



**Figure 9.** A general path graph and odd and even path graphs with the adopted vertex numberings.

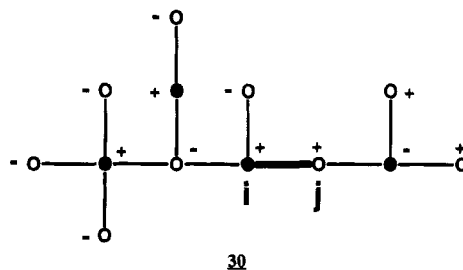
of (36) and (36a)). The atoms  $i$  and  $j$  having positive contributions are treated in corollary 2 as "zero" neighbors, i.e., they are included in the even-numbered neighbors.

The last two terms in eqs 36 and 36a are eliminated for acyclic structures as well as in many cases of cyclic ones for which the number of nonequivalent bonds does not exceed the number of nonequivalent atoms. In these cases, discussed below, any bond moment in the structure can be calculated solely from the atomic moments (any bond order can be determined solely from the partial atomic charges).

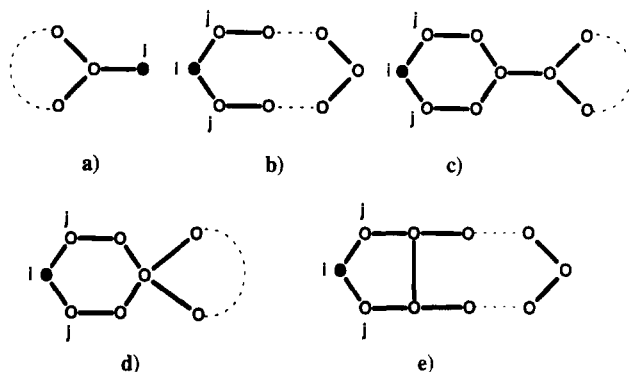
Jiang and Zhang<sup>30</sup> by using different SRW-based formalism obtained alternating connectivity effects on what they called point-energy or site reactivity in acyclic molecules. Formulas 35–36b offer a general solution for the alternating contributions to both atomic and bond moments of energy and the derived atomic charges and bond orders in any molecule or solid.

#### SOME SPECIFIC RELATIONSHIPS BETWEEN ATOMIC AND BOND MOMENTS OF ENERGY (BETWEEN TOPOLOGICAL BOND ORDERS AND TOPOLOGICAL ATOMIC CHARGES)

An essential difference between the topological bond orders ( $TBOs$ ) and the MO bond orders is that, as shown by eq 36,  $TBOs$  are determined by topological atomic charge ( $TACs$ ) contributions coming from all atoms in the structure but not only from the two atoms that form the bond. This is a natural consequence of the  $TBO$  definition which is based on self-returning walks traversing in many ways all atoms



**Figure 10.** A branched acyclic structure (tree graph). The alternating negative and positive contributions of the first-neighbor, second-neighbor, etc. to the bond order of the  $ij$  bond are shown.



**Figure 11.** Examples for the classes of molecules all topological bond orders ( $TBOs$ ) in which can be calculated from the topological atomic charges ( $TACs$ ): (a) branched cyclic; (b) monocyclic; (c) even-membered or even/odd-membered bridged bicyclic; (d) even-membered or even/odd-membered spiro bicyclic; and (e) fused odd-membered bicyclic.

and bonds. Our general eq 36 allowed the deriving of specific formulas for different classes of molecules and crystals. The equations presented deal with  $TBO/TAC$  relationships, but they are valid for the respective relationships between bond moments and atomic moments, as well. The results for the acyclic structures are particularly simple.

#### Linear acyclic structures (Path graphs)

$$p_{ij} = 2(f_i - f_{i-1} + f_{i-2} - \dots) \quad (37)$$

$$p_{ij} = (f_i - f_{i-1} + f_{i-2} - \dots) + (f_j - f_{j+1} + f_{j+2} - \dots) \quad (38)$$

For example,

$$p_{12} = 2f_1; \quad p_{23} = 2(f_2 - f_1); \quad p_{34} = 2(f_3 - f_2 + f_1); \dots \quad (39)$$

For  $n = \text{odd}$

$$p_{ij}(\text{central}) = f_i(\text{central}) \quad (40)$$

#### Branched acyclic structures (Tree graphs)

$$p_{ij} = (f_i - \sum_{h=i-1} f_h + \sum_{g=i-2} f_g - \sum_{f=i-3} f_f + \dots) + (f_j - \sum_{k=j+1} f_k + \sum_{l=j+2} f_l - \sum_{m=j+3} f_m + \dots) \quad (41)$$

**Cyclic Molecules.** To allow the finding of all specific  $TBO/TAC$  relationships by means of eqs 34 and 36 the molecule must incorporate at least one vertex which should be either terminal (vertex of degree one) in branched cyclic structures (Figure 11a) or symmetric "pseudoterminal" (vertex of degree two which is located at the end of graph

diameter and is incident to at least two equivalent bonds). The latter case refers, for example, to the monocyclic structures, even-membered or even/odd-membered bridged or spirolinked bicyclic ones, and odd-membered fused bicyclic ones (Figure 11b–e). Alternatively, when no terminal or pseudoterminal vertex is available, the molecule must contain a single central atom<sup>48,49</sup> incident to  $a_i$  equivalent bonds. Included here are, for example, the symmetrical bridged bicyclic and polycyclic molecules, bicyclic spirocompounds, and tricyclic fused or bridged ones (Figure 12a–d, respectively). In all such cases, eq 34 produces a formula for the TBO

$$p_{ij} = 2f_i/a_i \quad (42)$$

### Monocyclic molecules

$$p_{ij} = f_i = 1/n \quad (43)$$

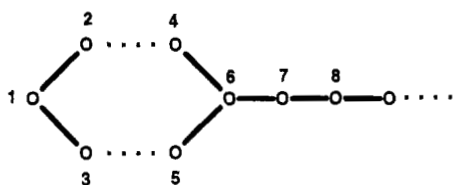
**Branched Monocyclic Molecules (Graphs 34–40 and 47–52, Figure 13).** Equation 41 and its specific cases eqs 37–39 hold for side-chain bonds, as well. The bond orders for the cyclic fragment are described in a similar alternating manner beginning with the pseudoterminal atom 1 for even-membered cycles (the first equalities 44–46) or, alternatively, beginning with the side-chain atoms (the second equalities 44–46), thus also covering the cases of odd-membered branched cycles

$$p_{12} = f_1 = f_2 + f_3 - f_4 - f_5 + f_6 - f_7 + \dots \quad (44)$$

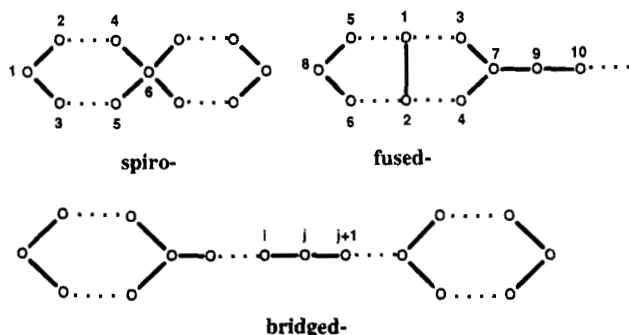
$$p_{24} = f_2 + f_3 - f_1 = f_4 + f_5 - f_6 + f_7 - \dots \quad (45)$$

$$p_{46} = f_4 + f_5 - f_2 - f_3 + f_1 = f_6 - f_7 + f_8 - \dots \quad (46)$$

Equations (45, 46, first equalities) are given for the case of a six-membered ring, but they can be readily written for any even-membered cycle.



**Spiro- and bridged bicyclic molecules containing even-membered or even/odd-membered rings and fused bicyclic molecules containing odd-membered or odd/even-membered rings (Graphs 44–46, 41–43, and 53–57 in Figure 13, respectively).**



Bonds 12, 24, and 46 in an even-membered spiro-linked ring are described by the same bond order formulas as given by the first part of eqs 44–46. The same holds for the even-membered bridged bicyclic molecules where new formulas are added only for the bonds  $ij$  belonging to the bridge. (The term “bridge” is used here in graph theoretical context as an edge or path connecting two isolated cycles but not in the meaning it has in chemical nomenclature).

$$p_{ij} = p_{jj+1} = f_j = f_i + f_{j+1} - \sum f_{i-1} - \sum f_{j+2} + \dots \quad (47)$$

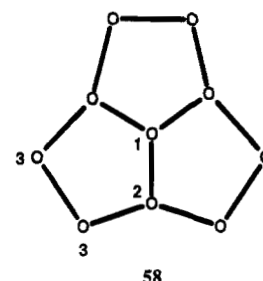
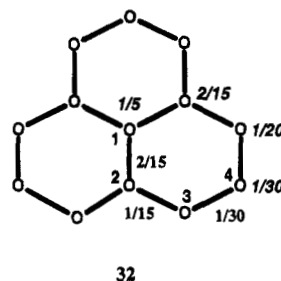
$$p_{ij} \neq p_{jj+1} = 2(f_i - \sum f_{i-1} + \sum f_{i-2} - \dots) \quad (48)$$

Equations 47 and 48 can also be used for calculating bond orders in linear polymers composed of bridged even-membered rings.

When dealing with fused odd-membered cycles (with or without branches), there are no bond terms in eq 36, and the bond order of the fusion site 1–2 is

$$p_{12} = f_1 + f_2 - f_3 - f_4 - f_5 - f_6 + f_7 + f_8 - f_9 + f_{10} \dots \quad (49)$$

### Peri-fused even-membered and/or odd-membered tricyclic molecules



Due to the threefold symmetry in these molecules, the condition for the ratio between the number of nonequivalent atoms and bonds is fulfilled and the following formulas were derived:

$$p_{12} = 2f_1/3 = 2f_2 - 2f_3 + f_4 \quad (50)$$

$$p_{23} = f_2 - f_1/3 = 2f_3 - f_4 \quad (51)$$

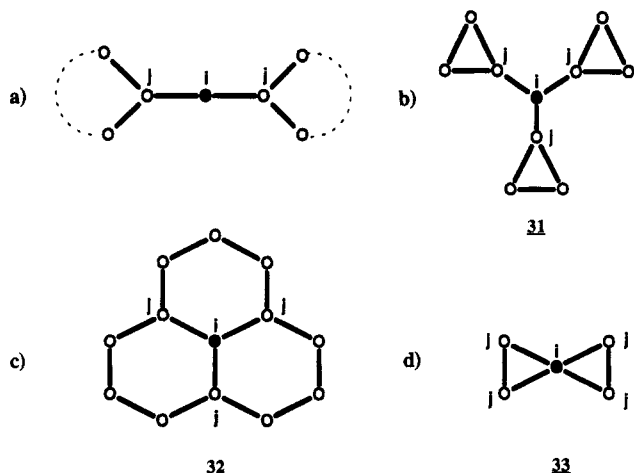
$$p_{34} = 2f_3 - f_2 + f_1/3 = f_4 \quad (52)$$

The first set of equalities 50–52 covers both cases of even- and odd-membered cycles (with  $p_{33}$  instead of  $p_{34}$  for the 5/5/5 case). In the molecules with even-membered cycles the presence of three equivalent terminal atoms in addition to the single central atom makes possible the second equalities 50–52 which actually coincide with the first equalities 46–44.

**Can explicit TBO/TAC relationships exist when the number of nonequivalent bonds exceeds that of nonequivalent atoms?**

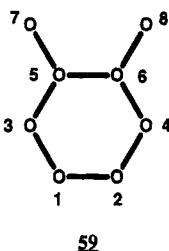
As mentioned in the foregoing, in some molecules two or more nonequivalent bonds may be “degenerate”, i.e., they may be characterized by the same bond moments. Thus, the number of nonequivalent bonds can be effectively reduced so as to not exceed that of the nonequivalent atoms.





**Figure 12.** Examples for the classes of symmetric molecules for which the presence of a single central atom allows the deriving of *TBO/TAC* relationships for all bonds: (a) linearly bridged bicyclic (polycyclic); (b) nonlinear bridged tricyclic; (c) peri-fused tricyclic; and (d) spiro bicyclic.

An example is presented below with graph **59** in which bonds 1–3 and 5–7 have the same moments. This reduces the number of different bond orders to that of the different atomic charges, and simple formulas result:  $p_{13} = p_{57} = 2f_7$ ;  $p_{12} = 2(f_1 - f_7)$ ;  $p_{35} = 2(f_3 - f_7)$ ;  $p_{56} = 2(f_5 - f_3)$ .



However, cases like those are relatively rare, and a lot of polycyclic molecules remain for which it is not possible to express each topological bond order in terms of the topological atomic charges of atoms only. Formula 36 has then to be used with all its terms, i.e., some bond orders are determined by all atomic charges and some other bond orders.

#### THE SRW-BASED ATOMIC AND BOND DESCRIPTORS AND CHEMICAL REACTIVITY

The limit distributions of the relative atomic and bond moments,  $f_i$  and  $p_{ij}$ , were interpreted in the foregoing as one-electron limit distributions over atoms and bonds or simply as one-electron contributions to atomic charges and bond orders, respectively. As shown in the preceding sections, these one-electron atomic and bond descriptors are graph invariants possessing important properties and manifesting interesting relationships. However, for practical purposes, it is crucial to verify to what extent these graph invariants could be used as indexes of reactivity in molecules.

In their important paper, Jiang and Zhang<sup>30</sup> made use of *SRWs* of length 2–12 to partition the  $\pi$ -electron energy into atomic and bond contributions which were regarded as measures for atom and bond reactivity. They offered an interesting interpretation of the reactivity of alternant conjugated molecules. Since all atoms in such molecules have

equal  $\pi$ -electronic charges, they regarded the atom with the highest energy to be the most reactive in substitution reactions.

This interpretation can be used in our approach as well because the relative atomic moments of energy can be interpreted as relative atomic energies and, though the formalism used is different, both approaches produce the same ordering of atoms in molecules and identify the same atoms as the most reactive ones.

Our finding<sup>32</sup> that relative atomic moments are equal to the respective squared coefficients in the principal eigenvector, however, allowed us to treat these graph invariants directly as atomic charges which we called topological atomic charges (*TAC*). These atomic descriptors were found to correlate linearly with  $r = 0.95$  to the *CNDO/2* charges of alkane atoms.<sup>50</sup> The potential use of the *TACs* in predicting reactivities in substitution reactions may be questioned because these are charges produced by the lowest occupied molecular orbital (*LOMO*). This is the most stable orbital, and, as well-known, reactivity is successfully predicted by frontier orbital charges. Unexpectedly enough, it seems that a certain correspondence exists between *LOMO* and frontier orbitals.<sup>51</sup> One of the manifestations of this correspondence seems to be a trend to relate the atoms with the extremum (highest or/and lowest) electron density in *LOMO* and *HOMO*, which would allow *TAC*-based predictions of reactivity in substitution reactions. For example, in polyenes the lowest *LOMO* charge corresponds to the highest *HOMO* one, whereas in polyacenes the highest *LOMO* and *HOMO* charges occur at the same bivalent atoms (Figure 14).

*TACs* seems to be also of potential use in predicting heteroatomic ring substitutions, according to the topological charge stabilization rule of Gimarc.<sup>52,53</sup> For example, *TACs* predict correctly the sulfur substitution to occur in position 1 but not in position 2 of pentalene (Figure 15).

The high *TAC* values, which result from the larger number of *SRWs* or electron trajectories, can also be interpreted as a higher degree of saturation of the respective atomic valencies. A more convenient measure of topological atomic valence (*TAV*) can be obtained from the *TACs* by analogy with the so-called *second moment scaling*,<sup>43</sup> i.e., from the second moment representation of all molecules as a standard state for their comparison (or, to paraphrase Gordon,<sup>54</sup> “a standard graph-like state of matter”). The second atomic moments are of particular importance, because they are proportional to the respective atomic valencies (or, in graph-theoretical language, the self-returning walks of length two are equal to the respective vertex degree:  $SRW^2_i = a_i$ ), while the second molecular moment is proportional to the doubled number of bonds  $E$  ( $SRW^2 = 2E$ ). Therefore, we can define the *TAVs* by multiplying the *TACs* (eqs 6) by the total number of self-returning walks of length two in the molecule:

$$TAV_i = f_i SRW^2 \quad (53)$$

The *TAV* atomic descriptor is a noninteger number close in value to the integers used for atomic valencies or for graph vertex degrees. The *TAVs* may be interpreted as atomic valencies corrected with accounting for all higher order atom–atom connectivities. Atoms with low *TAVs* are regarded to possess large free valence, and any radical

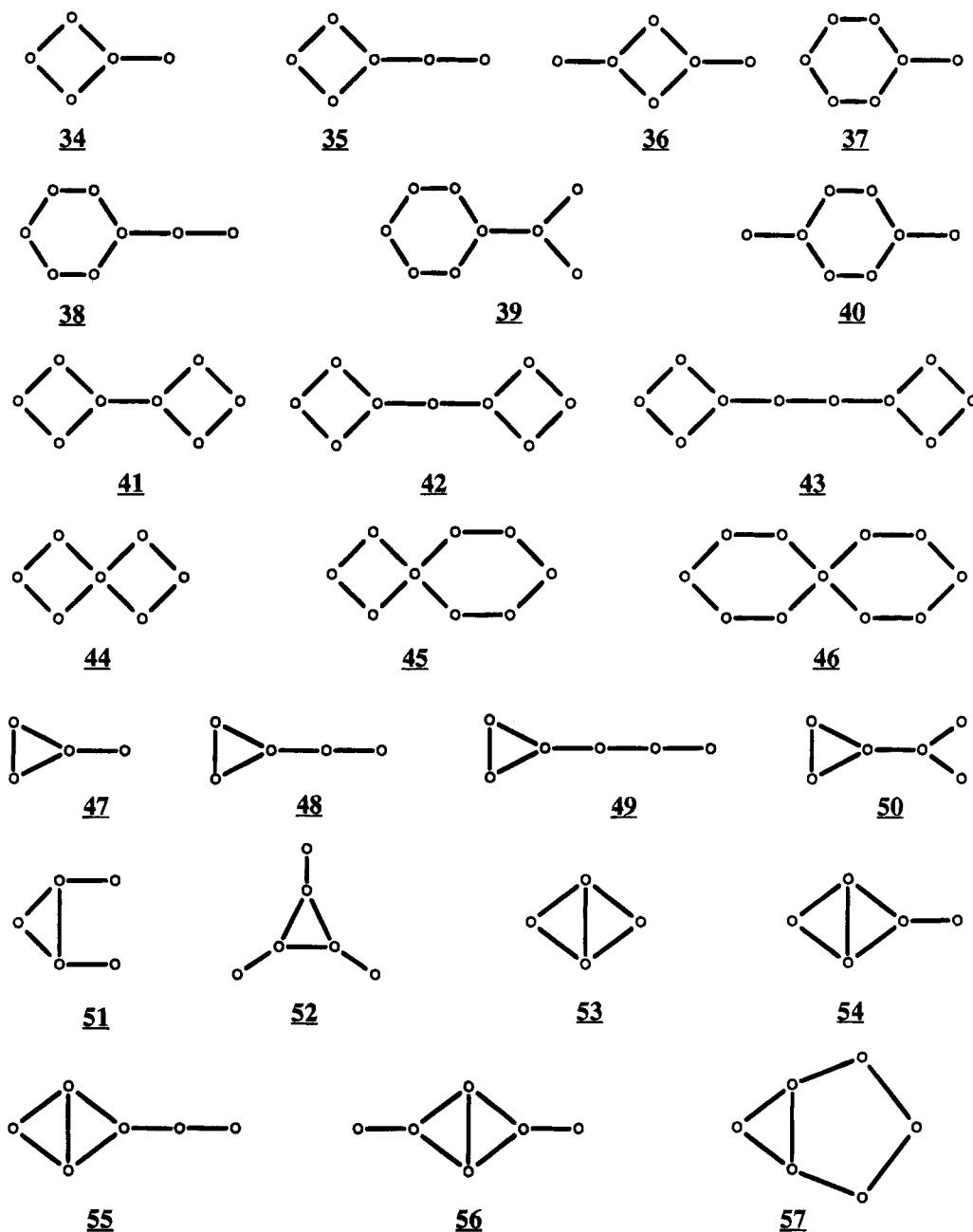


Figure 13. Molecular graphs of some classes of molecules for which simple *TBO/TAC* relationships exist.

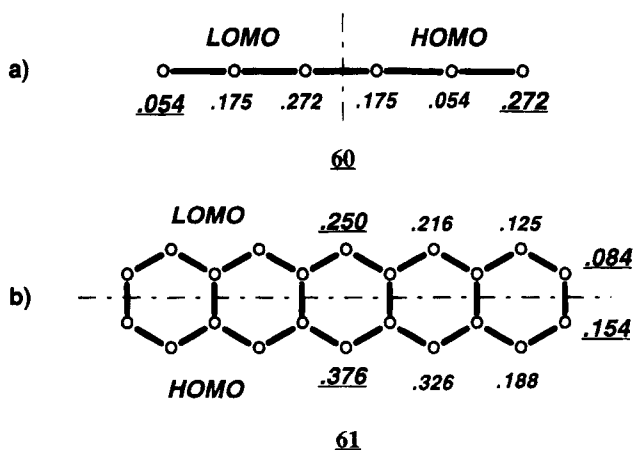


Figure 14. Correspondence of the extremum *LOMO* and *HOMO* atomic charges in (a)  $C_6$ -polyene and (b) pentacene.

addition reaction is predicted to proceed with the highest rate at the atom with the lowest *TAV* value.

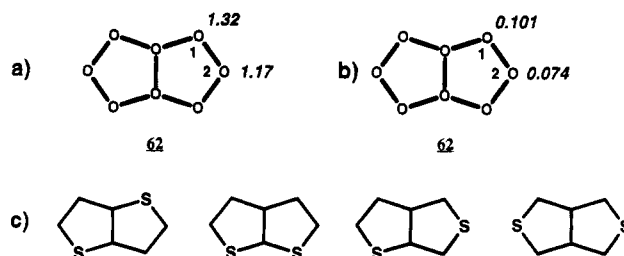


Figure 15. Both (a) PPP and (b) topological atomic charges predict correctly the more favorable position 1 for sulfur ring substitution in pentalene; (c) the four sulfur derivatives of pentalene ordered in a sequence of decreasing rate of formation reaction.

Analogously, the topological bond orders  $p_{ij}$  (eq 24) may be related to the degree of bond saturation and to the bond energy. Therefore, the higher this index, the less reactive the bond in bond cleavage reactions or in 1,2-addition reactions (or in 1,2-addition elementary steps producing reaction intermediates). The alternating atomic contributions

to the bond moments of energy can, on the other hand, be related to the Hückel  $4n + 2$ -rule. As seen in Figure 16, the  $4n + 2$ -atomic rings have more positive contributions and, therefore, higher bond moments, which stabilize such molecules as compared to the ones containing  $4n$ -rings.

Some more light is thus shed on the topological control of chemical reactivity. The Hückel method, which is the fundamental of the theory of chemical reactivity, is also topological in nature because it is based on the interactions between adjacent atoms (i.e., it implicitly makes use of self-returning walks of length two in molecular graphs). By making use of high order *SRWs*, our approach expands the molecular connectivity basis up to its convergence limit. Since it is the high atomic moments that determine the density of state of molecules and solids, the new reactivity indexes may be regarded as density-of-state-based molecular descriptors. In the next section we summarize the trends in molecular reactivity, and particularly those for addition reactions, as specified by the topological atomic valence and topological bond orders. The applicability of the *TACs* to atomic reactivity in substitution reactions is under study.<sup>53</sup>

### SOME TOPOLOGICAL RULES AND TRENDS OF MOLECULAR REACTIVITY

The generalized formulas 35a and 36 for the topological atomic charges and bond orders, combined with the definition of topological valence, allow us to introduce simple rules on chemical reactivity which agree with the experimental data. The first two alternating terms of each of these equations suffice to evaluate the major trends of atomic and bond reactivity, because it is normally the first and second neighbors that affect reactivity. Since the *TAVs* measure the saturated valence of atoms the inequalities derived show the reversed order of atomic reactivities.

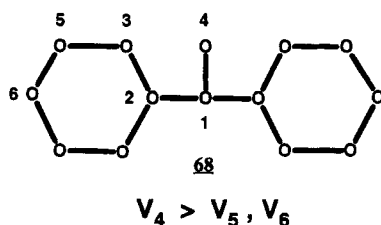
**Atomic Reactivity. Rule 1:** Atomic reactivity in a molecule increases with the decrease in atom adjacency:

$$V_{\text{primary}} < V_{\text{secondary}} < V_{\text{tertiary}} < V_{\text{quaternary}} \quad (54)$$

Here, *V* is used as an abbreviation for *TAV*. Inequalities 54 follow from the definition of *TAV* and inequalities 55 for the topological atomic charges

$$f_{\text{primary}} < f_{\text{secondary}} < f_{\text{tertiary}} < f_{\text{quaternary}} \quad (55)$$

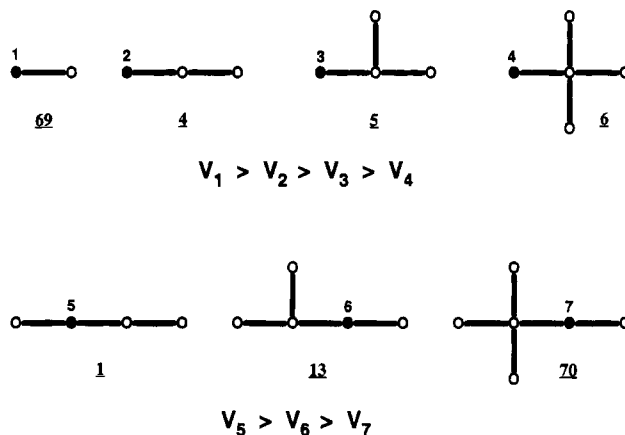
which we found earlier.<sup>31</sup> However, as mentioned in our earlier study, this inequality (whereas generally true for the second moments) is partially reversed in the higher moments of some molecules, due to the central location of an atom with lower connectivity and the peripheral location of an atom with higher connectivity. Thus, some peripheral secondary atoms may be predicted to be more reactive than some centrally located primary atoms, as presumed for atoms 5 and 6 versus atom 4 in graph 68.



**Rule 2:** Atomic reactivity in a molecule increases with the increase in the first neighbor adjacencies:

$$V_{i(1,2)} > V_{i(2,2)} > V_{i(2,3)} > V_{i(3,3)} \dots \quad (56)$$

Some examples are shown below.



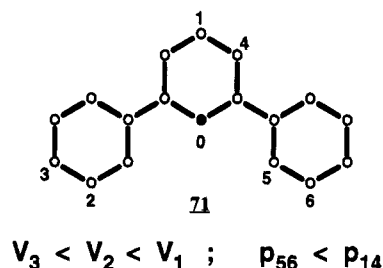
Once again, some of these inequalities could be overruled by the centrality factor.

**Rule 3:** The reactivity of atoms with the same valence and the same first neighbor adjacencies decreases with the increasing atom centrality  $c_i$

$$V_i(1) < V_i(2) < V_i(3) < \dots \quad (57)$$

for  $c_1 < c_2 < c_3 < \dots$ , and  $a_i = \text{const}$ ,  $a_{j(i)} = \text{const}$ .

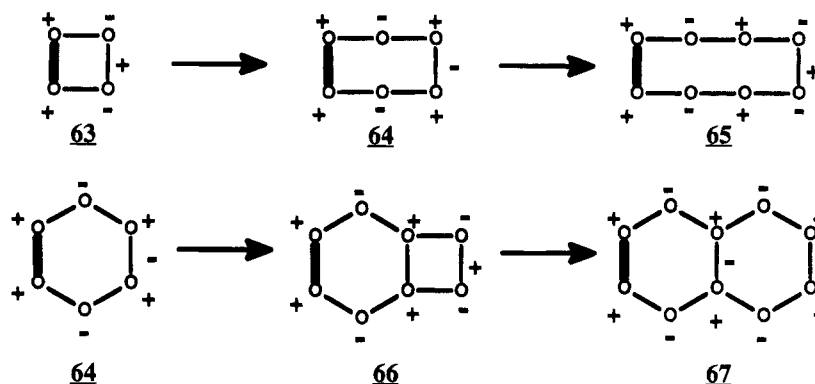
An example is shown below with graph 71 in which, at the same valence of the atoms and their first neighbors, centrality (determined with respect to the central atom 0) makes atom 3 the most reactive and atom 1 the least reactive one.



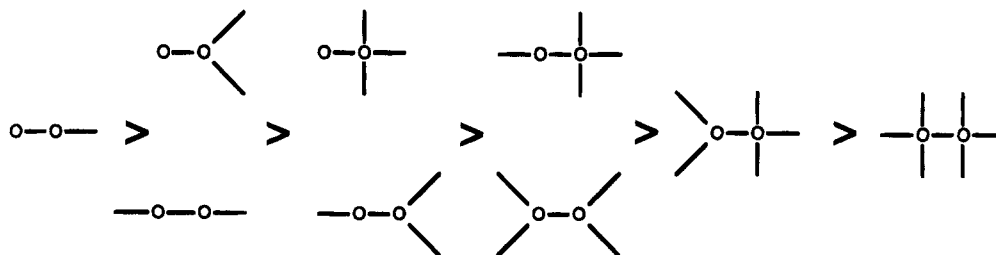
This rule follows from our previous finding<sup>31</sup> that while vertex adjacency is the major topological factor that affect *SRWs* the next factor of importance is vertex centrality,<sup>48,49</sup> i.e., the location of the vertex with respect to a uniquely specified graph center.

It should be mentioned that our rules 1 and 2 confirm with other means reactivity rules 1 and 2 of Jiang and Zhang<sup>30</sup> which are based on the point energies and agree with experimental facts. However, the centrality effects on atomic reactivity (our rule 3 and the exceptions of rules 1 and 2) seem to elude so far the attention of theoreticians. The predictions of such effects might be a challenge for experimental verification in chemical kinetics or synthetic organic chemistry.

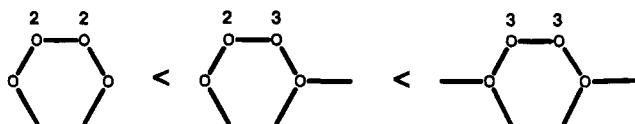
**Bond Reactivity.** Being based on the self-returning walks of the two atoms forming the bond, the rules on bond reactivity are analogous to those on atom reactivity.



**Figure 16.** The larger stability of  $4n + 2$  versus  $4n$   $\pi$ -bonded networks is due to the presence of more positive atomic moment contributions to the bond moments in the  $4n + 2$  molecules, as illustrated for one bond (thick line) in each molecule.



**Figure 17.** Bond reactivity decreases with the increase in the atom connectivity



**Figure 18.** Increasing reactivity of the 2–2 bond with the increase in the valence of the first neighboring atoms.

**Rule 4:** Bond reactivity decreases with the increase in the atom adjacencies (Figure 17).

$$V_{1-2} < \frac{V_{1-3}}{V_{2-2}} < \frac{V_{1-4}}{V_{2-3}} < \frac{V_{2-4}}{V_{3-3}} < V_{3-4} < V_{4-4} \quad (58)$$

Exceptions from rule 4 should be expected, due to centricity effects in large molecules.

**Rule 5:** The reactivity of bonds formed by atoms of the same adjacencies decreases with their first neighbors adjacencies (Figure 18).

$$V_{ij}(p(i), q(j)) > V_{ij}(r(i), s(j)) \quad (59)$$

for  $a_p, a_q > a_r, a_s$ .

Our rules 4 and 5, though based on different formalism, confirm reactivity rules 3 and 4 of Jiang and Zhang<sup>30</sup> who showed that one can thus identify the shortest bonds in benzenoid hydrocarbons which are those bonds at which 1,2-addition reactions occur.

**Rule 6:** At the same bond adjacencies the bond reactivity decreases with bond centricity

$$V_{ij}(1) < V_{ij}(2) < V_{ij}(3) < \dots \quad (60)$$

for  $a_{ij}(1) = a_{ij}(2) = a_{ij}(3) = \dots$  and  $c(1) < c(2) < c(3) < \dots$

An example is given with graph 71 in the foregoing where bonds 14 and 56 have the same adjacencies (2,3) but the more central 14 bond has higher bond order and is less reactive than the more peripheral bond 56. (Centrality is specified as the average of the distances from both bond ends to the central vertex 0.)

Due to the difficulties in specifying precisely the same atomic environment, rule 6, as well as rule 3, should however be regarded rather as general trends from which exceptions might occur.

In conclusion, we may summarize that our approach reveals molecular reactivity as being topologically controlled to a higher degree than previously supposed. Work is in progress on further development of the topological chemical reactivity and, particularly, on its interplay with frontier orbital theory.<sup>51</sup>

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