Atomic Branching in Molecules

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ABSTRACT: A graph theoretic measure of extended atomic branching is defined that accounts for the effects of all atoms in the molecule, giving higher weight to the nearest neighbors. It is based on the counting of all substructures in which an atom takes part in a molecule. We prove a theorem that permits the exact calculation of this measure based on the eigenvalues and eigenvectors of the adjacency matrix of the graph representing a molecule. The definition of this measure within the context of the Hückel molecular orbital (HMO) and its calculation for benzenoid hydrocarbons are also studied. We show that the extended atomic branching can be defined using any real symmetric matrix, as well as any Hermitian (self-adjoint) matrix, which permits its calculation in topological, geometrical, and quantum chemical contexts. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 106: 823–832, 2006

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Introduction

Many properties of an atom in a molecule are determined mainly by its nearest-neighbor atoms [e.g., nuclear magnetic resonance (NMR) chemical shifts, atomic charges]. This is one of the reasons we refer in chemistry, for instance, to carbon atoms as primary, secondary, tertiary, or quaternary, depending on the number of substituents that are different from hydrogen of the corresponding atom. A quaternary carbon atom is, for instance, a carbon atom bonded to four other atoms different from hydrogen; i.e., it

has four nearest neighbors. This terminology refers to the degree of branching of an atom in a molecule, understanding it as the number of atoms that are different from hydrogen bonded to an atom; incidentally, this is known in graph theory as the degree of a vertex or graph theoretical valence [1]. Many properties depend on the atomic branching of a carbon atom. Thus, for example, Wiener [2] was prompted to search for a quantitative structure–property relationship by qualitative statements found in chemical texts of the day that the boiling points of alkanes are related to branching of their molecular skeletons. No attempts were presented in those early days to describe or characterize molecular branching. Similarly, it is well known that the stability of the

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carbocations generated from primary, secondary, tertiary, and quaternary carbon atoms are of a different order of magnitude [3]. However, the properties of atoms in a molecule are also affected by the second nearest-neighbor atoms, i.e., the atoms bonded to its nearest neighbors. Take, for instance, a primary carbon atom that is bonded to a quaternary, a tertiary or a secondary carbon. In the first case, it has only one second nearest neighbor, but this number increases up to four in the last case affecting its atomic properties in a different way. This situation demonstrates that the concept of atomic branching based only on the nearest neighbors of an atom is not appropriate to describe a number of atomic properties. This has been the motivation of the use of augmented valence as a complexity index for molecules [4–6].

This idea of augmented vertex (atom) branching extends beyond atoms in molecules and is also applicable to other systems represented by complex networks [7–10]. Although in a complex network most effects are transmitted from one element to another through the link joining them together, it is obvious that this effect can reach topologically distant elements by following a path of inter-element links [11, 12]. Thus, if we consider two elements with the same number of connections, the one having the larger number of second nearest neighbors will have a greater chance of receiving an information flow through the network than the other. The "value" of this information can decreases as the length of the path increases (think of "value" in terms of time delay), which make closest neighbors more important than the more distant ones. This is well known by organic chemists who have studied the transmission of inductive effects through molecular backbones to explain molecular reactivity [13].

In the search for such extended atomic branching we desire a property that accounts for the effects of all atoms in the molecule giving higher weight to the closest ones. It is also desired that this property can be generalized to different representations of a molecule and not be limited to one or another of such representations, e.g., graph-theoretic, quantum chemical, geometric. In the present work, we introduce a measure of extended atomic branching that fulfill these requirements. It is based on counting all substructures in which an atom takes part in a molecule. We prove a theorem that permits the exact calcu-

lation of this measure based on the eigenvalues and eigenvectors of the adjacency matrix of the graph representing this molecule. The definition of this measure within the context of the Hückel molecular orbital (HMO) and its calculation for benzenoid hydrocarbons is also studied. We show that the extended atomic branching can be defined using any real symmetric matrix, and show examples of this generalization to geometric matrices. In the last section of this work we prove that the extended atomic branching can be defined by using any Hermitian (self-adjoint) matrix, which permits its calculation in quantum chemical contexts.

Extending Atomic Branching to Long-Range Contributions

In the intuitive and simple idea of branching of an atom i, defined as the number of atoms different of hydrogen bonded to i, we only consider the number η_0 of its closest neighbors: $B(i) = \eta_0$. In other words, η_0 is the number of bonds involving the corresponding atom i; i.e., its vertex degree δ_i in graph theoretic terminology. If we want to generalize this approach by considering all subgraphs in which the vertex i participates, we have to use a more general expression for atomic branching, such as

$$EB(i) = \eta_0 + \kappa_1\eta_1 + \kappa_2\eta_2 + \cdots + \kappa_n\eta_n, \quad (1)$$

where the terms $\kappa_k\eta_k$ can be considered as correction factors accounting for longer-range effects to the branching of the vertex i. The average over all the vertices' branching can be used as a criterion of molecular branching. This idea follows the pioneering work of Ruch and Gutman [14], who introduced partial ordering of graphs according to the "degree of branching," which was then extended by Michalski [15] discussing possible connections between branching extent and spectra of trees. Another version based on partial order was also analyzed by Klein and Babić [16], which is in some way related to our current "higher-order" extension of the concept of branching.

Mathematically, vertex degrees can be obtained as the main diagonal elements of the second power of the adjacency matrix of the graph [17]. Consequently, the original definition of branching of an atom can be expressed as follows:

$$V(i) = \left(\mathbf{A}^2\right)_{ii} = \left[\begin{array}{c} i \\ \bullet\!\!-\!\!-\!\!-\!\! \end{array}\right]. \qquad (2)$$

In general, the ith diagonal entry of the kth power of the adjacency matrix can be expressed as a linear combination of different subgraphs containing the vertex i [18]. For instance, the ith element of the main diagonal of the third power of the adjacency matrix counts twice the number of triangles containing vertex i and the ith diagonal element of the fourth power of the adjacency matrix counts the number of times vertex i takes place in certain subgraphs as follows:

$$\left(\mathbf{A}^3\right)_{ii} = 2\left[\begin{array}{c} i \\ \bullet\!\!\triangleleft \end{array}\right] \qquad (3)$$

$$\left(\mathbf{A}^4\right)_{ii} = \left[\begin{array}{c} i \\ \bullet\!\!-\!\!-\!\! \end{array}\right] + \left[\begin{array}{c} i \\ \bullet\!\!\wedge\!\!\searrow \end{array}\right] + 2\left[\begin{array}{c} i \\ \wedge\!\!\searrow \end{array}\right] + 2\left[\begin{array}{c} i \\ \square \end{array}\right]. \qquad (4)$$

Then, if we take a linear combination of these diagonal entries of the adjacency matrix and arrange them properly, we can express branching defined by expression (1) in terms of powers of the adjacency matrix:

$$EB(i) = C_0(\mathbf{A}^0)_{ii} + C_1(\mathbf{A}) + C_2(\mathbf{A}^2)_{ii} + C_3(\mathbf{A}^3)_{ii}$$
$$+ C_4(\mathbf{A}^4)_{ii} + \cdots + C_k(\mathbf{A}^k)_{ii}. \qquad (5)$$

Substituting the expressions of main diagonal entries by their linear combinations in terms of subgraphs, we have

$$EB(i) = C_0 + C_2\left\{\left[\begin{array}{c} i \\ \bullet\!\!-\!\!-\!\! \end{array}\right]\right\} + C_3\left\{2\left[\begin{array}{c} i \\ \bullet\!\!\triangleleft \end{array}\right]\right\} +$$
$$C_4\left\{\left[\begin{array}{c} i \\ \bullet\!\!-\!\!-\!\! \end{array}\right] + \left[\begin{array}{c} i \\ \bullet\!\!\wedge\!\!\searrow \end{array}\right] + 2\left[\begin{array}{c} i \\ \wedge\!\!\searrow \end{array}\right] + 2\left[\begin{array}{c} i \\ \square \end{array}\right]\right\} + \cdots, \qquad (6)$$
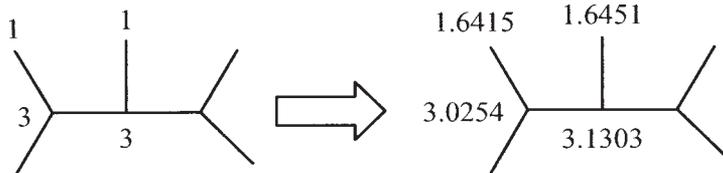
where the term in brackets accompanying the coefficient C_0 is equal to one, i.e., the atom i, and the coefficient C_1 is only present in the case where the graph has weighted vertices. After appropriate rearrangement we obtain expression (1), now written in graphic form:

$$EB(i) = \kappa_0\left[\begin{array}{c} i \\ \bullet\!\!-\!\!-\!\! \end{array}\right] + \kappa_1\left[\begin{array}{c} i \\ \bullet\!\!\triangleleft \end{array}\right] + \kappa_2\left[\begin{array}{c} i \\ \bullet\!\!\wedge\!\!\searrow \end{array}\right] +$$
$$\kappa_3\left[\begin{array}{c} i \\ \wedge\!\!\searrow \end{array}\right] + \kappa_4\left[\begin{array}{c} i \\ \square \end{array}\right] + \cdots, \qquad (7)$$

where the coefficients κ_i are combinations of coefficients used in (6).

We can think about this process as an optimization in which we transform an atomic branching index based only on contributions coming from adjacent atoms into another that also considers contributions from "higher-order" substructures. For instance, if we consider the graph representing 1,2,3-trimethylpentane, which has five vertices of degree one and three vertices of degree three, and calculate the first 10 powers of the adjacency matrix we obtain the vertex degrees shown below at the right:

Here we used the expression like (5) with $k = 10$. We can select the coefficients such that larger substructures receive less weight in the linear combination than the smaller ones. For mathematical convenience (see further discussion), we have selected these coefficients as $C_k = 1/k!$, obtaining the above results for 1,2,3-trimethylpentane.

Extended Atomic Branching: Mathematical Formulation

Mathematically, the terms $(\mathbf{A}^k)_{ii}$ represent the number of closed walks (CWs) of length k, also known as self-returning walks, that start and end at the atom i [19, 20]. A walk of length k is a sequence of (not necessarily different) atoms $\nu_1, \nu_2, \ldots, \nu_r, \nu_{r+1}$, such that for each $i = 1, 2, \ldots, N$ there is a link from ν_i to ν_{i+1}. A closed walk (CW) is a walk in which $\nu_{r+1} = \nu_1$ [20]. The number of CWs starting (and ending) at atom i can be expressed in terms of the spectral properties of the molecular graph [21]:

$$\mu_k(i) = (\mathbf{A}^k)_{ii} = \sum_{j=1}^{N} [\nu_j(i)]^2 (\lambda_j)^k, \qquad (8)$$

where λ_j is the jth eigenvalue of the adjacency matrix and $\nu_j(i)$ is the ith component of the eigenvector associated with the jth eigenvalue.

It is then easy to realize that the approach we previously used to extend the atomic branching in order to account for larger substructures in the molecule is given by

$$EB(i) = \sum_{k=0}^{\infty} \frac{\mu_k(i)}{k!}. \qquad (9)$$

Let λ_1 be the main (the principal or the leading) eigenvalue of $\mathbf{A}$. For any non-negative integer k and any $i \in \{1, \ldots, N\}$, $\mu_k(i) \leq \lambda_1^k$, series $\sum_{k=0}^{\infty} [\mu_k(i)/k!]$, whose terms are non-negative, converges:

$$EB(i) \leq \sum_{k=0}^{\infty} \frac{\lambda_1^k}{k!} = e^{\lambda_1}. \qquad (10)$$

The following result shows that $EB(i)$ can be obtained mathematically from the spectra of the adjacency matrix of the molecular graph [22].

Theorem 1. Let $G = (V, E)$ be a simple molecular graph of order N. Let $\nu_1, \nu_2, \ldots, \nu_N$ be an orthonormal basis of $\mathfrak{R}^N$ composed of eigenvectors of $\mathbf{A}$ associated with the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_N$. Let $\nu_j(i)$ denote the ith component of ν_j. For all $i \in V$, the atomic extended branching may be expressed as follows:

$$EB(i) = \sum_{j=1}^{N} [\nu_j(i)]^2 e^{\lambda_j}. \qquad (11)$$

Proof. The orthogonal projection of the unit vector e_i (the ith vector of the canonical base of $\mathfrak{R}^N$) on ν_j is

$$p_j(e_i) = \frac{\langle e_i, \nu_j \rangle}{\|\nu_j\|^2} \nu_j = \langle e_i, \nu_j \rangle \nu_j = \nu_j(i) \cdot \nu_j. \qquad (12)$$

Hence, the number of CWs starting at atom i can be expressed in terms of the spectral properties of the graph as follows:

$$\mu_k(i) = (\mathbf{A}^k)_{ii} = \langle \mathbf{A}^k e_i, e_i \rangle = \left\langle \mathbf{A}^k \sum_{j=1}^{N} p_j(e_i), \sum_{j=1}^{N} p_j(e_i) \right\rangle$$

$$= \sum_{j=1}^{N} (\lambda_j)^k [\nu_j(i)]^2. \quad (13)$$

Then, using our expression defining the extended atomic branching $EB(i) = \sum_{k=0}^{\infty} [\mu_k(i)/k!]$, we obtain

$$EB(i) = \sum_{k=0}^{\infty} \left\{ \sum_{j=1}^{N} \frac{(\lambda_j)^k [\nu_j(i)]^2}{k!} \right\}. \quad (14)$$

By reordering the terms of series (11), we obtain the absolutely convergent series:

$$\sum_{j=1}^{N} \left\{ [\nu_j(i)]^2 \sum_{k=0}^{\infty} \frac{(\lambda_j)^k}{k!} \right\} = \sum_{j=1}^{N} [\nu_j(i)]^2 e^{\lambda_j}, \quad (15)$$

which obviously also converges to $EB(i)$. Thus, the result follows and expression (11) is an exact formula for calculating the extended branching of an atom represented by a molecular graph.

Extended Atomic Branching in the HMO Context

We begin by considering conjugated molecules using the HMO approach [23]. The normalized linear combination of atomic orbitals (LCAO) wave function of the jth molecular orbital (MO) of the π-electronic system of a conjugated hydrocarbon with N carbon atoms is given by

$$\varphi_j = \sum_{j=1}^{N} C_j(i) \chi_i. \quad (16)$$

The energy of the jth orbital is the expectation value for the one-electron effective Hamiltonian $\hat{\mathbf{H}}$:

$$\varepsilon_j = \langle \varphi_j | \hat{\mathbf{H}} | \varphi_j \rangle. \quad (17)$$

By assuming equal values, respectively, for all the Coulomb, and all the nonzero resonance integrals, the energy of ith orbital is expressed as

$$\varepsilon_j = \alpha + \beta \lambda_j, \quad (18)$$

where λ_j is the jth eigenvalue of the adjacency matrix, $\mathbf{A}$, of the molecular graph representing the hydrogen-depleted skeleton of the hydrocarbon. The total π-electron energy satisfies the relation

$$E = \sum_{j=1}^{N} |\lambda_j|. \quad (19)$$

The kth spectral moment of the adjacency matrix of the molecular graph is then

$$\mu_k = \sum_{j=1}^{N} (\lambda_j)^k = \int_{-\infty}^{+\infty} x^k \Gamma(x) dx, \quad (20)$$

where $\Gamma(x) = \sum_{j=1}^{N} \delta(x - \lambda_j)$ is the spectral density functional, and $\delta(x)$ is the Dirac function. A physical interpretation for a CW in a conjugated hydrocarbon can be provided by an analogy with the spectral moments of the spectral density in a Hubbard model in a lattice [24]. A CW of length k is characterized by the following steps: (i) remove an electron from atom $\vec{0}$ leaving a hole, (ii) move the hole by exchanging its place with adjacent electrons that carry their spins with them; and (iii) after k steps, replace the first electron (with its spin) in the hole at atom $\vec{R} \equiv \vec{0}$, completing the closed walk. The final spin configuration must then coincide with the initial one. Thus, the infinite sum $\sum_{k=0}^{\infty} \mu_k(i)$ corresponds to the number of times in which a π-electron at atom i moves back and forward visiting the other atoms in the molecule. We will consider that the larger this number, the larger the electron density at the corresponding atom as a consequence of the "longer permanence" of this electron at the corresponding atom. It is also straightforward to realize that the "topological time" in which the electron completes a CW is directly related to its length. Thus, the shorter the CW, the shorter the time in which the electron returns to the atom, which immediately implies a longer permanence of the electron in such atom. This intuition indicates that the shorter CWs will have more influence in the electron density of atom n than the larger ones, which correspond exactly to our formulation of the extended valence using the expression

$$\sum_{k=0}^{\infty} \frac{\mu_k(i)}{k!}.$$

In the HMO context with $\alpha = 0$ and $\beta = 1$, the extended atomic branching is given by

$$EB(i) = \sum_{j=1}^{N} [C_j(i)]^2 e^{\varepsilon_j}. \qquad (21)$$

This formula can also be expressed in terms of occupied and vacant molecular orbitals:

$$EB(i) = \sum_{j}^{OCC} [C_j(i)]^2 e^{\varepsilon_j} + \sum_{j}^{VAC} [C_j(i)]^2 e^{\varepsilon_j}. \qquad (22)$$

Extended Atomic Branching for Benzenoid Hydrocarbons

A CW is called odd (even) if k is odd (even). It is also easy to show that

$$EB(i) = \sum_{j=1}^{N} [C_j(i)]^2 \cosh(\varepsilon_j) + \sum_{j=1}^{N} [C_j(i)]^2 \sinh(\varepsilon_j)$$

$$= EB_{even}(i) + EB_{odd}(i), \qquad (23)$$

which means that the term $EB_{odd}(i)$ only accounts for substructures containing at least one odd cycle. Benzenoid polycyclic aromatic hydrocarbons do not contain odd cycles, and consequently their molecular graphs are bipartite [25]. A graph is bipartite if its vertex set V can be partitioned into two subsets V_1 and V_2, such that all edges have one endpoint in V_1 and the other in V_2. In such cases, it is obvious that

$$EB(i) = EB_{even}(i) = \sum_{j=1}^{N} [C_j(i)]^2 \cosh(\varepsilon_j). \qquad (24)$$

In the case of bipartite molecules, such as benzenoid hydrocarbons, it is well known that the spectrum is symmetric, i.e., $\varepsilon_j = -\varepsilon_{N-j+1}$ [25]. We will then have the following expression for the extended atomic branching:

$$EB(i) = 2 \sum_{j}^{OCC} [C_j(i)]^2 \cosh(\varepsilon_j). \qquad (25)$$

Table I gives the values of the extended valence for the carbon atoms of seven benzenoid hydrocar-

TABLE I

Values of extended atomic branching calculated by the graph-theoretic method in the present work and by extended Hückel method and DFT calculations.

Compound	$EB(i)$	EHT	Ab initio
Benzene	2.2800	2.032	
Naphthalene			
1	2.2846	2.043	
2	2.3387	2.052	
3	3.1409	2.943	
Phenanthrene			
1	3.2004	2.960	
2	2.3405	2.057	
3	2.2846	2.041	
4	2.2846	2.044	
5	2.3387	2.049	
6	3.1428	2.954	
7	2.3405	2.054	
Anthracene			
1	2.2846	2.042	1.961
2	2.3387	2.048	1.974
3	3.1428	2.947	2.952
4	2.3947	2.074	2.014
Pyrene			
1	3.1447	2.952	
2	2.3406	2.045	
3	2.3389	2.054	
4	2.2863	2.034	
5	3.2623	2.978	
Chrysene			
1	2.3405	2.059	
2	3.2004	2.962	
3	3.2023	2.968	
4	3.2023	2.968	
5	2.3423	2.064	
6	2.3406	2.057	
7	3.1428	2.953	
8	2.3387	2.050	
9	2.2846	2.044	
10	2.2846	2.042	
Naphthacene			
1	2.2846	2.042	
2	2.3387	2.050	
3	3.1428	2.952	
4	2.3947	2.078	
5	3.1447	2.951	
R		0.998	0.998

bons (see Fig. 1). We have previously considered that a CW in a conjugated hydrocarbon can represent the moving back and forward of the π-elec-
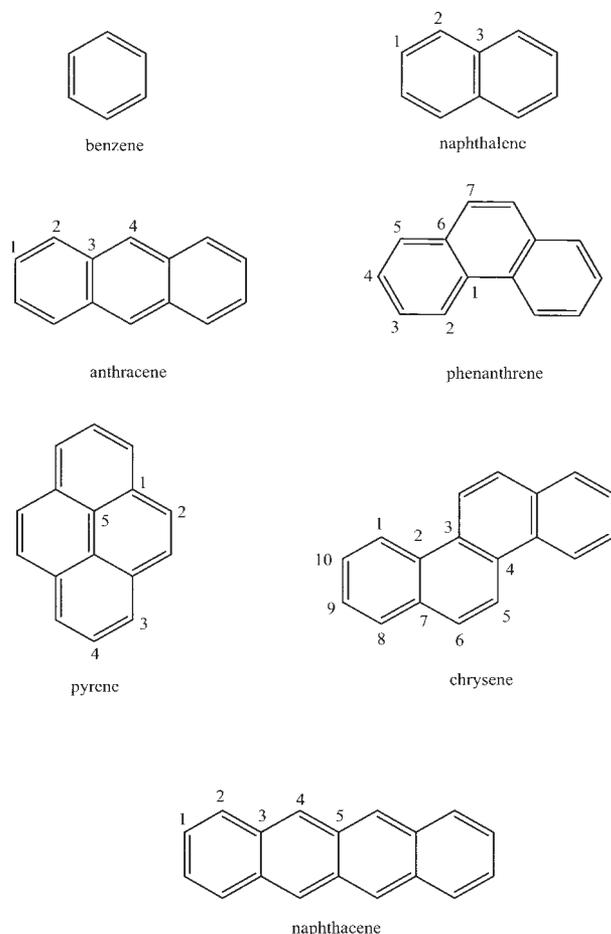
FIGURE 1. Molecular structures of polycyclic aromatic benzenoid compounds studied.

atoms as [26]: $EB_{EHT}(i) = B(i) - q_{EHT}(i)$. For the case of anthracene, we have also defined an ab initio extended valence using DFT calculations at cc-pVDZ B3LYP level reported by Dessent [27]: $Eb_{DFT}(i) = B(i) - q_{DFT}(i)$. As can be seen in both cases the extended atomic branching defined from graph spectra shows very good linear correlations with those obtained from quantum chemical atomic charges, which indicates that, at least for polycyclic benzenoid hydrocarbons, the extended branching brings important electronic and topological molecular information.

## Extended Atomic Branching Beyond Simple Graphs

In the previous section, we have limited our discussion to a purely graph theoretic context based on the use of the adjacency matrix of a molecular graph. However, it would be of great theoretical and practical importance to expand the concept of extended atomic branching beyond the use of adjacency matrix and to account for other graph theoretic as well as quantum chemical matrices. Theorem 1 is also true for real symmetric matrices (the proof is similar to the one given below and will be not shown here). Thus, we will illustrate a couple of examples of extending the concept used to develop characterization of atomic branching for this kind of matrices. The

trons through the carbon–carbon skeleton. In this case, it is justified to express the extended branching as the sum of two terms, one coming from the nearest neighbors of atom i and the other coming from long-range contributions. We can then consider the first term as the number of conjugated bonds incident to atom i, i.e., atom degree, and the second term as the correction introduced by the electron motion along the different longer substructures of the molecule. By full analogy with the definition of atomic charge density, we will write $EB(i) = B(i) - q(i)$, where $B(i) = \delta_i$ is the number of conjugated bonds incident to i, and $q(i)$ is a type of topological charge produced by the motion of π-electrons through the carbon–carbon skeleton of the molecule.

As a consequence of this interpretation, we have calculated the extended Hückel theory (EHT) extended valences for the same carbon

TABLE II

Values of the extended branching index calculated from the weighted adjacency matrices of *n*-butane, 2-butene, and 2-butyne.

Weighted adjacency matrix	Extended atomic branching
$\mathbf{A} = \begin{pmatrix} 0 & 1.54 & 0 & 0 \\ 1.54 & 0 & 1.54 & 0 \\ 0 & 1.54 & 0 & 1.54 \\ 0 & 0 & 1.54 & 0 \end{pmatrix}$	4.8128 2.7581
$\mathbf{A} = \begin{pmatrix} 0 & 1.52 & 0 & 0 \\ 1.52 & 0 & 1.34 & 0 \\ 0 & 1.34 & 0 & 1.52 \\ 0 & 0 & 1.52 & 0 \end{pmatrix}$	4.1012 2.6248
$\mathbf{A} = \begin{pmatrix} 0 & 1.46 & 0 & 0 \\ 1.46 & 0 & 1.20 & 0 \\ 0 & 1.20 & 0 & 1.46 \\ 0 & 0 & 1.46 & 0 \end{pmatrix}$	3.5572 2.4340

TABLE III

Values of the extended branching index calculated from the D/D matrices for two conformational isomers of 1,3-butadiene.

s-*cis* isomer	s-*trans* isomer

$$D/D = \begin{pmatrix} 0 & 1.342 & 1.179 & 0.933 \\ 1.342 & 0 & 1.344 & 1.179 \\ 1.179 & 1.344 & 0 & 1.342 \\ 0.933 & 1.179 & 1.342 & 0 \end{pmatrix} \qquad D/D = \begin{pmatrix} 0 & 1.342 & 1.179 & 1.198 \\ 1.342 & 0 & 1.344 & 1.179 \\ 1.179 & 1.344 & 0 & 1.342 \\ 1.198 & 1.179 & 1.342 & 0 \end{pmatrix}$$

9.263

10.777

11.003

11.621
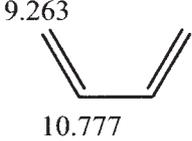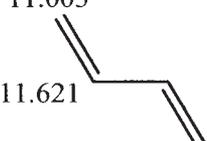
first corresponds to a weighted graph in which edges are weighted by bond lengths. Let r_{ij} be the bond distance for the bond between atoms i and j. The elements of the adjacency matrix of the weighted graph are then defined as follows:

$$a_{ij} = \begin{cases} r_{ij} & \text{if } i \text{ and } j \text{ are adjacent} \\ 0 & \text{otherwise.} \end{cases}$$

Table II illustrates the adjacency matrices and the extended atomic branching for the carbon atoms of *n*-butane, 2-butene, and 2-butyne. It can be seen that the values decrease from the alkane to the alkyne for both the methyl group and the carbon with different hybridizations: $C_{sp_3} > C_{sp_2} > C_{sp}$. It is worth noting that this approach permits the differentiation of heteroatoms in the molecular structure and it is also applicable in the HMO context for hetero-conjugated molecules [23].

The second example given here is concerned with the so-called D/D matrices [28]. These matrices are defined for molecular graphs of given fixed geometry. Matrix element (i, j) is given as the quotient of the Euclidean (through space) distance between atoms i and atom j and the graph theoretical distance between the same two atoms (through bonds), which is given by the number of bonds between the atoms. The leading eigenvalue of the D/D matrix in the case of chain structures has been interpreted as a measure of the degree of chain folding, because in more folded structures there will be a larger number of smaller matrix elements, resulting in a smaller magnitude of the leading eigenvalue. Besides being used for characterization of small molecules, D/D matrices and the degree of folding of proteins [29, 30] D/D matrices

offered a way for the characterization of general non-chain structures [31], including polyhedral structures [32] and even more realistic molecular models based on representation of atoms by overlapping spheres having van der Waals radii [33]. More recently, D/D matrices have been used not only for numerical characterizations of DNA in which individual DNA sequences are represented by a set of matrix invariants but also for numerical characterization of proteomics maps [34].

Table III illustrates the D/D matrices and the extended atomic branching for two conformational isomers of 1,3-butadiene, namely s-*cis* and s-*trans* isomers. The values of the extended branching for the carbon atoms are lower for the s-*cis* isomer that for the s-*trans*, which also coincides with the previous example, in which the molecules with shorter bond distances showed smaller $EB(i)$ values. These values differ significantly from the values of $EB(i)$ obtained before from the adjacency matrices. The main idea of this section is that we can extend the definition of extended atomic branching to any representation of the graph by means of real symmetric matrices.

Extended Atomic Branching From Hermitian Matrices

A square matrix is called Hermitian if it is self-adjoint. Therefore, a Hermitian matrix $\mathbf{A} = (a_{ij})$ is defined as one for which $\mathbf{A} = \mathbf{A}^H$, where $\mathbf{A}^H$ denotes the conjugate transpose. Hereafter, $|a|$ and $\bar{a}$ indicate the modulus and the complex conjugate of a. Thus, in a Hermitian matrix, $a_{ij} = \bar{a}_{ji}$ and their diagonal elements are real. It is of common use to

represent observables by Hermitian matrices/operators in quantum mechanics. We recall that Hermitian matrices are unitarily diagonalizable, and they have real eigenvalues. Then, the use of Hermitian operators/matrices to represent observables guarantees that the outcome of observations is real [35].

For a graph $G = (V, E)$, we define a complex function $\varphi : V \times V \to C$ such that, $f(u, u) \in R$, $f(u, v) \neq 0$ if and only if u and v are adjacent, and $f(u, v) = \overline{f(v, u)}$. In such conditions we define the Hermitian adjacency matrix of G as $\mathbf{H}_{ij} = f(v_i, v_j)$. So, the matrix $\mathbf{H}$ is Hermitian, justifying the terminology used.

That is, the Hermitian extended branching of atom i in the molecule is given by

$$EB(i) = \sum_{k=0}^{\infty} \frac{(\mathbf{H}^k)_{ii}}{k!}. \quad (26)$$

Let λ be the main eigenvalue of $\mathbf{H}$. For any non-negative integer k and any $i \in \{1, \dots, n\}$, $\mu_k(i) \leq \lambda^k$, series (2), whose terms are non-negative, converges:

$$\sum_{k=0}^{\infty} \frac{(\mathbf{H}^k)_{ii}}{k!} \leq \sum_{k=0}^{\infty} \frac{\lambda^k}{k!} = e^{\lambda}. \quad (27)$$

Thus, the Hermitian extended valence of any atom i is bounded above by $EB(i) \leq e^{\lambda}$.

Theorem 2. Let $\mathbf{H}$ be the Hermitian (adjacency) matrix associated with the graph $G = (V, E)$ of order N. Let $v_1, v_2, \dots, v_N$ be an orthonormal basis of C^N composed of eigenvectors of $\mathbf{H}$ associated with the eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_N$. Let v_j^i denote the ith component of v_j. For all $i \in V$, the Hermitian extended branching can be expressed as follows:

$$EB(i) = \sum_{j=1}^{N} |v_j^i|^2 e^{\lambda_j}. \quad (28)$$

Proof. The orthogonal projection of the unit vector e_i (the ith vector of the canonical base of R^n) on v_j is

$$pr_j(e_i) = \frac{\langle e_i, v_j \rangle}{\|v_j\|^2} v_j = \langle e_i, v_j \rangle v_j = \overline{v_j^i} \cdot v_j. \quad (29)$$

Hence,

$$(\mathbf{H}^k)_{ii} = \langle \mathbf{H}^k e_i, e_i \rangle = \left\langle \mathbf{H}^k \sum_{j=1}^{N} pr_j(e_i), \sum_{j=1}^{N} pr_j(e_i) \right\rangle$$

$$= \sum_{j=1}^{N} \lambda_j^k |v_j^i|^2. \quad (30)$$

Using expression (26), we obtain

$$EB(i) = \sum_{k=0}^{\infty} \left(\sum_{j=1}^{N} \frac{\lambda_j^k |v_j^i|^2}{k!} \right). \quad (31)$$

By reordering the terms of series (31), we obtain the absolutely convergent series:

$$\sum_{j=1}^{N} \left(\left| v_j^i \right|^2 \sum_{k=0}^{\infty} \frac{\lambda_j^k}{k!} \right) = \sum_{j=1}^{N} |v_j^i|^2 e^{\lambda_j}, \quad (32)$$

which obviously also converges to $EB(i)$.

In the present work, we will not provide any calculation result for the application of these matrices in defining the extended atomic branching in a context of quantum chemistry, as these calculations will be detailed in a separate publication. However, it is straightforward to realize the new avenues that Theorem 2 opens for extending this context in a quantum chemical context.

Conclusions

We have introduced a measure that extend the concept of atomic branching beyond the traditional consideration of the nearest-neighbor atoms. The idea is that the atomic branching of an atom depends not only on its closest neighbors, but also on atoms that are separated at topological distances larger than one. The influence of an atom on the atomic branching of another decreases as the number of bonds separating them increases. The way in which we introduce this atomic branching permits its exact calculation from the spectrum of the adjacency matrix of the molecular graph. However, we have shown that this approach is applicable to other molecular representations, which include the use of Hermitian matrices as those used in quantum chemistry to represent observables.

The atomic branching index developed here show some interesting and desirable characteristics. It is known that in complex systems the relation-

ships between elements are both short range and long range. One atom receives "information" from near neighbors by means of short-range direct local interactions. However, this information can travel from one atom to another, having an indirect influence on all other atoms. This characteristics is well accounted for by the atomic branching index, which takes into account both short-range and long-range interactions in a hierarchical way, in which the first receive more weight than the second. The other characteristic of the branching degree that merits some attention is that it is not obtained as the simple sum of the different parts of the system, but it is defined on the basis of global topological properties of the molecule. In a complex system, there is a sense that the different elements cannot "know" what is happening in the system as a whole. On the contrary, all the complexity of the system would be deduced from the complexity of such single element. In other words, the molecular complexity is created by the interrelationships between the atoms and not by a simple sum of individual atomic properties. Both characteristics suggest that the augmented atomic branching is a good characterization of the level of complexity of an atom, a characteristic that will be analyzed in future work.

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