Walking Backward: Walk Counts of Negative Order

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A closed formula is derived for walk counts of negative order k in a graph or molecule, as defined recently by Lukovits and Trinajstić. Some unexpected observations made by these authors easily follow from this formula. Gratifyingly, the formula is very similar to the one obtained earlier for usual walk counts. Moreover, while for walk counts of $k \rightarrow +\infty$ the numerically largest eigenvalue of the adjacency matrix plays an important part, for walk counts of $k \rightarrow -\infty$ the numerically smallest eigenvalue plays a corresponding part.

INTRODUCTION

The counts of walks of a particular length (or order) k ($k = 1, 2, ...$) in graphs are valuable atomic and molecular descriptors.[1−5] The count of walks of order k from vertex i to vertex j is given by the i,j-element of the kth power $\mathbf{A}^k$ of the adjacency matrix $\mathbf{A}$ of a graph (a molecule),[6,7] while the number of walks of order k from vertex i to all other vertices, $awc_k(i)$, can be obtained as the sum of walk counts of order $k-1$ of all neighbors of i (the Morgan algorithm).

The concept of walks was recently extended by Lukovits and Trinajstić in this journal to walks of zero and negative orders.[8] These authors in order to obtain walk counts of order k ($k \leq 0$) formally applied in the backward direction both methods mentioned above. Being concerned mostly with example graphs (molecules) rather than with a general formula, they made some in part unexpected observations: (1) While usual walk counts are positive integers, atomic and molecular walk counts of zero and negative order as a rule are noninteger and even negative numbers. (2) Though the assumption of all atomic walk counts of order zero to be equal to 1 always results in correct walk counts of positive orders, for some graphs atomic walk counts of order zero, as obtained through the backward Morgan algorithm, are not equal to 1. (3) Though the atomic and molecular walk counts for $k \rightarrow -\infty$ converge to zero for some graphs, for others they diverge.

By a mathematical technique called spectral decomposition we earlier derived a nonrecursive equation for walk counts of positive order.[9−12] Now by the same technique we obtain a corresponding formula for walk counts of zero and negative order, from which all the unexpected observations mentioned above follow easily.

RESULTS AND DISCUSSION

Let $\mathbf{A}$ be the adjacency matrix of a simple connected undirected graph G with n vertices. $\mathbf{A}^k$ then is the kth power of $\mathbf{A}$. Further let $\lambda_1 > \lambda_2 \geq ... \geq \lambda_n$ be the eigenvalues of $\mathbf{A}$, and let $\{\mathbf{x}_1, ..., \mathbf{x}_n\}$ be an orthonormal basis of eigenvectors $\mathbf{x}_i$ of $\mathbf{A}$, where $\mathbf{x}_i$ is the eigenvector associated with λ_i. The coefficients of $\mathbf{x}_j$ are denoted as $\mathbf{x}_{ji}$ ($i = 1, ..., n$). Then for $j = 1, ..., n$ and $k = 1, 2, 3, ...$, we have

$$\mathbf{A}^k\mathbf{x}_j = \lambda_j{}^k\mathbf{x}_j \tag{1}$$

Further, let

$$s_j = \Sigma_{i=1,n}\mathbf{x}_{ji} \tag{2}$$

be the sum of coefficients of the jth eigenvector.[13] Then[10] for the vector of ones, denoted as $\mathbf{1} = (1, ..., 1)^T$

$$\mathbf{1} = \Sigma_{j=1,n}s_j\mathbf{x}_j \tag{3}$$

holds. For $k \geq 1$ the sequence of atomic walk count vectors is given as

$$\mathbf{a}_k = \mathbf{A}^k\,\mathbf{1} = \Sigma_{j=1,n}s_j\mathbf{A}^k\mathbf{x}_j = \Sigma_{j=1,n}s_j\lambda_j{}^k\mathbf{x}_j \tag{4}$$

In particular, $\mathbf{a}_1 = \Sigma s_j\lambda_j\mathbf{x}_j$ is the vector of degrees.

The basic idea of our approach for "inverting" the Morgan algorithm is the following. The adjacency matrix $\mathbf{A}$ has a certain rank r ($0 \leq r \leq n$). This rank corresponds to the number of eigenvalues (counted with their multiplicity) which are different from zero. The r-dimensional subspace generated by the corresponding eigenvectors will be referred to as the subspace generated by $\mathbf{A}$. Then $\bar{\mathbf{A}}$, defined as $\mathbf{A}$ restricted to this subspace, is nonsingular, and therefore its inverse $\bar{\mathbf{A}}^{-1}$ exists within this subspace. $\bar{\mathbf{A}}^{-1}$ is naturally continued on the whole space by assigning $\mathbf{0}$ to the elements of the null-space of $\mathbf{A}$. Vectors $\mathbf{a}_0$, $\mathbf{a}_{-1}$, $\mathbf{a}_{-2}$, $\mathbf{a}_{-3}$ ... can be obtained by repeated application of the so defined $\bar{\mathbf{A}}^{-1}$ to $\mathbf{a}_1$, the vector of degrees.

Initially, we define a sequence of sets $\mathbf{A}^{-k}(\mathbf{a}_1)$ ($k = 0, 1, 2, ...$) by letting

$$\mathbf{A}^{-k}(\mathbf{a}_1) = \{\mathbf{y} \in I\!R^n:\ \mathbf{A}^k\mathbf{y} = \mathbf{a}_1\} \tag{5}$$

Generally, $\mathbf{A}^{-1}(\mathbf{a}_1) \neq \varnothing$, because $\mathbf{A1} = \mathbf{a}_1$ and therefore $\mathbf{1} \in \mathbf{A}^{-1}(\mathbf{a}_1)$. If $\mathbf{A}$ is nonsingular, the inverse of $\mathbf{A}$ exists and

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each set $\mathbf{A}^{-k}(\mathbf{a}_1)$ contains exactly one element. If $\mathbf{A}$ is singular, the sets $\mathbf{A}^{-k}(\mathbf{a}_1)$ are affine subspaces of $\mathbb{R}^n$.

For a fixed k, we define another set by letting

$$\mathbf{A}(\mathbf{A}^{-k}(\mathbf{a}_1)) = \{\mathbf{z} \in \mathbb{R}^n : \text{ There exists } \mathbf{y} \in \mathbf{A}^{-k}(\mathbf{a}_1) \text{ with } \mathbf{Ay} = \mathbf{z}\} \quad (6)$$

It follows that

$$\mathbf{A}(\mathbf{A}^{-k}(\mathbf{a}_1)) \subseteq \mathbf{A}^{-(k-1)}(\mathbf{a}_1) \quad (7)$$

while the opposite inclusion is not necessarily true.[14] A counterexample for $k = 2$ is given in case 3 in the paper by Lukovits and Trinajstić,[8] where $\mathbf{1} \in \mathbf{A}^{-1}(\mathbf{a}_1)$ (as is generally the case), but $\mathbf{1} \notin \mathbf{A}(\mathbf{A}^{-2}(\mathbf{a}_1))$.

To finally obtain the sequence $\mathbf{a}_0$, $\mathbf{a}_{-1}$, $\mathbf{a}_{-2}$, $\mathbf{a}_{-3}$, ..., we first construct the sets $\mathbf{A}^{-k}(\mathbf{a}_1)$ by spectral decomposition. In general, these sets contain an infinite number of elements, not all of which are in the desired Morgan sequence. Second, we construct the sets $\mathbf{A}(\mathbf{A}^{-k}(\mathbf{a}_1))$. We will see that each of the latter sets contains no more than one element, which is $\mathbf{a}_{-(k-2)}$.

Construction of $\mathbf{A}^{-k}$ $(\mathbf{a}_1)$. Let a vector $\mathbf{y} \in \mathbb{R}^n$ be represented as a linear combination of the basis eigenvectors $\mathbf{x}_1$, ..., $\mathbf{x}_n$ by

$$\mathbf{y} = \Sigma_{j=1,n} y_j \mathbf{x}_j \quad (8)$$

Then

$$\mathbf{A}^k\mathbf{y} = \Sigma_{j=1,n} y_j \lambda_j^k \mathbf{x}_j \quad (9)$$

Now $\mathbf{y}$ is an element of the set $\mathbf{A}^{-k}(\mathbf{a}_1)$, iff $\mathbf{A}^k\mathbf{y} = \mathbf{a}_1$ holds, which is equivalent to

$$\Sigma_j y_j \lambda_j^k \mathbf{x}_j = \Sigma_j s_j \lambda_j \mathbf{x}_j \quad (10)$$

So by comparing the coefficients, we see that $\mathbf{A}^{-k}(\mathbf{a}_1)$ consists of all vectors $\mathbf{y}$ with

$$y_j = \begin{cases} s_j/\lambda_j^{k-1} & \text{where } \lambda_j \neq 0 \\ \text{arbitary} & \text{where } \lambda_j = 0 \end{cases} \quad (11)$$

If $\mathbf{A}$ has rank r, the dimension of $\mathbf{A}^{-k}(\mathbf{a}_1)$ is $n - r$.

Construction of $\mathbf{A}(\mathbf{A}^{-k}(\mathbf{a}_1))$. Motivated by eq 11, we define the set of indices belonging to nonzero eigenvalues

$$J = \{j:\ 1 \leq j \leq n \text{ and } \lambda_j \neq 0\} \quad (12)$$

For $\mathbf{y} \in \mathbf{A}^{-k}(\mathbf{a}_1)$ it is immediately seen that

$$\mathbf{Ay} = \Sigma_{j \in J} (s_j/\lambda_j^{k-2})\, \mathbf{x}_j \quad (13)$$

Therefore we can define $\mathbf{a}_{-(k-2)} = \mathbf{Ay}$ as the uniquely determined and only element of $\mathbf{A}(\mathbf{A}^{-k}(\mathbf{a}_1))$.[15] In particular, for $k = 2$ we have $\mathbf{a}_0 = \Sigma_{j \in J} s_j \mathbf{x}_j$. Because of eq 3, $\mathbf{1} = \Sigma_{j=1,n} s_j \mathbf{x}_j$, summed over *all* indices, $\mathbf{a}_0$ can be regarded as the projection of $\mathbf{1}$ onto the r-dimensional subspace generated by $\mathbf{A}$. In the case of nonsingular $\mathbf{A}$ (case 1 in ref 8), $\mathbf{a}_0 = \mathbf{1}$ holds. In case 2 in ref 8, $\mathbf{A}$ is singular, but $\mathbf{1}$ nevertheless is included in the subspace generated by $\mathbf{A}$, because those s_j which correspond to eigenvalue zero are zero themselves, whence $\mathbf{a}_0 = \mathbf{1}$ holds in this case also.

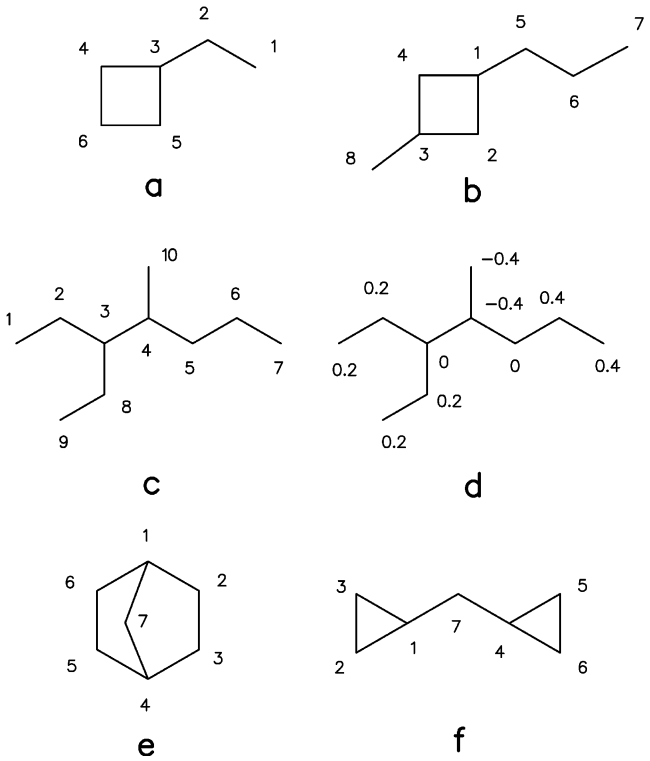

Figure 1. Some molecular graphs mentioned in the text with arbitrary vertex numbering.

Definition of Sequence $\mathbf{a}_0$, $\mathbf{a}_{-1}$, $\mathbf{a}_{-2}$, $\mathbf{a}_{-3}$, ... Let

$$\mathbf{a}_0 = \Sigma_{j \in J} s_j \mathbf{x}_j \quad (14)$$

(where the summation is done as above over indices belonging to nonzero eigenvalues), and in general ($k \geq 0$)

$$\mathbf{a}_{-k} = \Sigma_{j \in J} s_j \lambda_j^{-k} \mathbf{x}_j \quad (15)$$

Thus $\mathbf{a}_{-k}$ can be computed directly without recursion in full analogy to (4), and we immediately see the validity of the Morgan recursion for walk counts of negative order also

$$\mathbf{A}(\mathbf{a}_{-k}) = \Sigma_{j \in J} s_j \lambda_j^{-(k-1)} \mathbf{x}_j = \mathbf{a}_{-(k-1)} \quad (16)$$

Equations 15 and 16 hold for both positive and negative integers k, including zero.

We developed a computer program applicable to any simple connected undirected graph (chemically, any saturated hydrocarbon). The program calculates, based on eq 15, all awc_{-k} values (the coefficients of $\mathbf{a}_{-k}$) and their sum over all vertices, mwc_{-k}, for k up to a certain limit. Table 1 shows the results for three examples (two of which are taken from ref 8), the graphs of ethylcyclobutane (Figure 1a, Table 1a), 4-methyl-3-ethylheptane (Figure 1c,d, Table 1b), and dicyclopropylmethane (Figure 1f, Table 1c).

The Behavior of $\mathbf{a}_{-k}$ for $k \rightarrow \infty$. Lukovits and Trinajstić mentioned the seemingly irregular converging (or not so) behavior of awc_{-k} for $k \rightarrow \infty$ of various molecular graphs.[8] In this section we derive that the behavior of awc_{-k} for $k \rightarrow \infty$ is predictable once the eigenvalues and eigenvectors are known.

The behavior of $\mathbf{a}_k$ of positive order for $k \rightarrow \infty$ was discussed earlier.[10] Generally, for a nonbipartite graph the normalized $\mathbf{a}_k$ converge to the principal eigenvector, belong-

Table 1. Eigenvalues, Eigenvector Coefficient Sums, awc_k and mwc_k Values for Zero and Negative Orders for the Graphs of (a) Ethylcyclobutane, (b) 4-Methyl-3-ethylheptane, and (c) Both Bicyclo[2.2.1]heptane and Dicyclopropylmethane

(a) ethylcyclobutane

eigenvalues	−2.175	−1.126	0.000	0.000	1.126	2.175	
eigenvector coeff sums	0.098	0.131	0.577	0.000	0.467	2.328	
	vertex						
iteration k	1	2	3	4	5	6	mwc_k
0	0.667	1.000	1.333	1.000	1.000	0.667	5.667
−1	0.333	0.667	0.667	0.333	0.333	0.333	2.667
−2	0.333	0.333	0.333	0.167	0.167	0.000	1.333
−3	0.167	0.333	0.167	0.000	0.000	0.000	0.667
−4	0.222	0.167	0.111	0.000	0.000	−0.111	0.389
−5	0.111	0.222	0.056	−0.056	−0.056	−0.056	0.222
−6	0.167	0.111	0.056	−0.028	−0.028	−0.111	0.167
−7	0.083	0.167	0.028	−0.056	−0.056	−0.056	0.111
−8	0.130	0.083	0.037	−0.028	−0.028	−0.093	0.102
−9	0.065	0.130	0.019	−0.046	−0.046	−0.046	0.074
−10	0.102	0.065	0.028	−0.023	−0.023	−0.074	0.074
−11	0.051	0.102	0.014	−0.037	−0.037	−0.037	0.056
−12	0.080	0.051	0.022	−0.019	−0.019	−0.059	0.057
−13	0.040	0.080	0.011	−0.029	−0.029	−0.029	0.043
−14	0.063	0.040	0.017	−0.015	−0.015	−0.046	0.045
−15	0.032	0.063	0.008	−0.023	−0.023	−0.023	0.034
−16	0.050	0.032	0.013	−0.012	−0.012	−0.037	0.035
−17	0.025	0.050	0.007	−0.018	−0.018	−0.018	0.027
−18	0.039	0.025	0.011	−0.009	−0.009	−0.029	0.028
−19	0.020	0.039	0.005	−0.014	−0.014	−0.014	0.021
−20	0.031	0.020	0.008	−0.007	−0.007	−0.023	0.022

(b) 4-Methyl-3-ethylheptane

eigenvalues	−2.149	−1.543	−1.000	−1.000	0.000	0.000	1.000	1.000	1.543	2.149	
eigenvector coeff sums	0.145	−0.149	0.000	0.000	−0.496	0.919	−0.892	0.072	0.298	2.824	
	vertex										
iteration k	1	2	3	4	5	6	7	8	9	10	mwc_k
0	0.545	1.000	1.455	1.000	1.182	1.000	0.818	1.000	0.545	0.364	8.909
−1	0.364	0.545	0.636	0.364	0.455	0.818	0.545	0.545	0.364	−0.091	4.545
−2	0.256	0.364	0.289	−0.091	0.298	0.545	0.521	0.364	0.256	−0.223	2.579
−3	0.231	0.256	0.132	−0.223	0.107	0.521	0.438	0.256	0.231	−0.331	1.620
−4	0.204	0.231	0.052	−0.311	0.082	0.438	0.439	0.231	0.204	−0.357	1.195
−5	0.205	0.204	0.026	−0.357	0.027	0.439	0.411	0.204	0.205	−0.384	0.981
−6	0.198	0.205	0.007	−0.384	0.025	0.411	0.414	0.205	0.198	−0.389	0.889
−7	0.200	0.198	0.005	−0.389	0.007	0.414	0.404	0.198	0.200	−0.396	0.841
−8	0.198	0.200	0.000	−0.396	0.009	0.404	0.405	0.200	0.198	−0.397	0.821
−9	0.200	0.198	0.001	−0.397	0.002	0.405	0.401	0.198	0.200	−0.399	0.809
−10	0.199	0.200	−0.001	−0.399	0.003	0.401	0.402	0.200	0.199	−0.399	0.805
−11	0.200	0.199	0.000	−0.399	0.001	0.402	0.400	0.199	0.200	−0.400	0.802
−12	0.200	0.200	−0.001	−0.400	0.001	0.400	0.401	0.200	0.200	−0.400	0.801
−13	0.200	0.200	0.000	−0.400	0.000	0.401	0.400	0.200	0.200	−0.400	0.801
−14	0.200	0.200	0.000	−0.400	0.000	0.400	0.400	0.200	0.200	−0.400	0.800
−15	0.200	0.200	0.000	−0.400	0.000	0.400	0.400	0.200	0.200	−0.400	0.800

(c) Dicyclopropylmethane

eigenvalues	−1.814	−1.000	−1.000	−1.000	0.471	2.000	2.343	
eigenvector coeff sums	0.272	0.000	0.000	0.000	0.223	0.000	2.622	
	vertex							
iteration k	1	2	3	4	5	6	7	mwc_k
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	7.000
−1	0.500	0.500	0.500	0.000	0.500	0.500	0.500	3.000
−2	0.500	0.500	0.000	−0.500	0.000	0.500	0.500	1.500
−3	0.750	0.750	−0.250	−1.500	−0.250	0.750	0.750	1.000
−4	1.500	1.500	−0.750	−3.250	−0.750	1.500	1.500	1.250
−5	3.125	3.125	−1.625	−7.000	−1.625	3.125	3.125	2.250
−6	6.625	6.625	−3.500	−14.875	−3.500	6.625	6.625	4.625
−7	14.062	14.062	−7.437	−31.625	−7.437	14.062	14.062	9.750
−8	29.875	29.875	−15.812	−67.187	−15.812	29.875	29.875	20.687

ing to the largest eigenvalue λ_1 of **A**. For bipartite graphs, however, the sequence diverges if $s_n \neq 0$, so that there are two sequences, one for odd and another for even k, both converging to a linear combination of the principal eigenvector and the eigenvector belonging to the smallest eigenvalue $\lambda_n = -\lambda_1$. Here we derive analogous formulas for $\mathbf{a}_{-k}$.

First, we consider the Euclidean norm ("length") of the vectors $\mathbf{a}_{-k}$, which is given by

$$||\mathbf{a}_{-k}|| = (\Sigma_{j\in J} s_j^2 \lambda_j^{-2k})^{0.5} \quad (17)$$

where J is defined as above, eq 12. From now on we consider

Table 2. Some Examples, Most Taken from Ref 8, of Molecular Graphs Displaying Various Limiting Behavior of Walk Counts for $k \rightarrow -\infty$

general cases		examples				
case	limes of $\|\|a_{-k}\|\|$	name	figure	table	eigenvalues λ with $\|\lambda\| = \lambda_0$	limes of $a_{-k}/\|\|a_{-k}\|\|$
$\lambda_0 > 1$	0	ethylcyclobutane	1a, 2a	1a	± 1.12603	alternating linear combinations of eigenvectors (see Table 1a)
		cyclopentane			$2 (= \lambda_1)$	principal eigenvector
		2-methylpropane			$\pm 1.73205 (= \lambda_1)$	alternating linear combinations of eigenvectors
		n-pentane			$\pm 1.73205 (= \lambda_1)$	alternating linear combinations of eigenvectors
$\lambda_0 = 1$	0.816	2,3-dimethylbutane			-1	eigenvector belonging to $\lambda = -1$ with alternating sign
	0.894	4-methyl-3-ethylheptane	1c, 1d, 2c	1b	1 (double)	an eigenvector belonging to $\lambda = 1$ (see Table 1b)
$\lambda_0 < 1$	∞	*n*-butane			-0.61803	eigenvector belonging to -0.61803 with alternating sign
		dicyclopropylmethane	1f, 2d	1c	0.47068	eigenvector belonging to 0.47068 (see Table 1c)
		bicyclo[2.2.1]heptane	1e, 2d		0.47068	eigenvector belonging to 0.47068
		propyl-3-methylcyclobutane	1b, 2b		± 0.78014	alternating linear combinations of eigenvectors

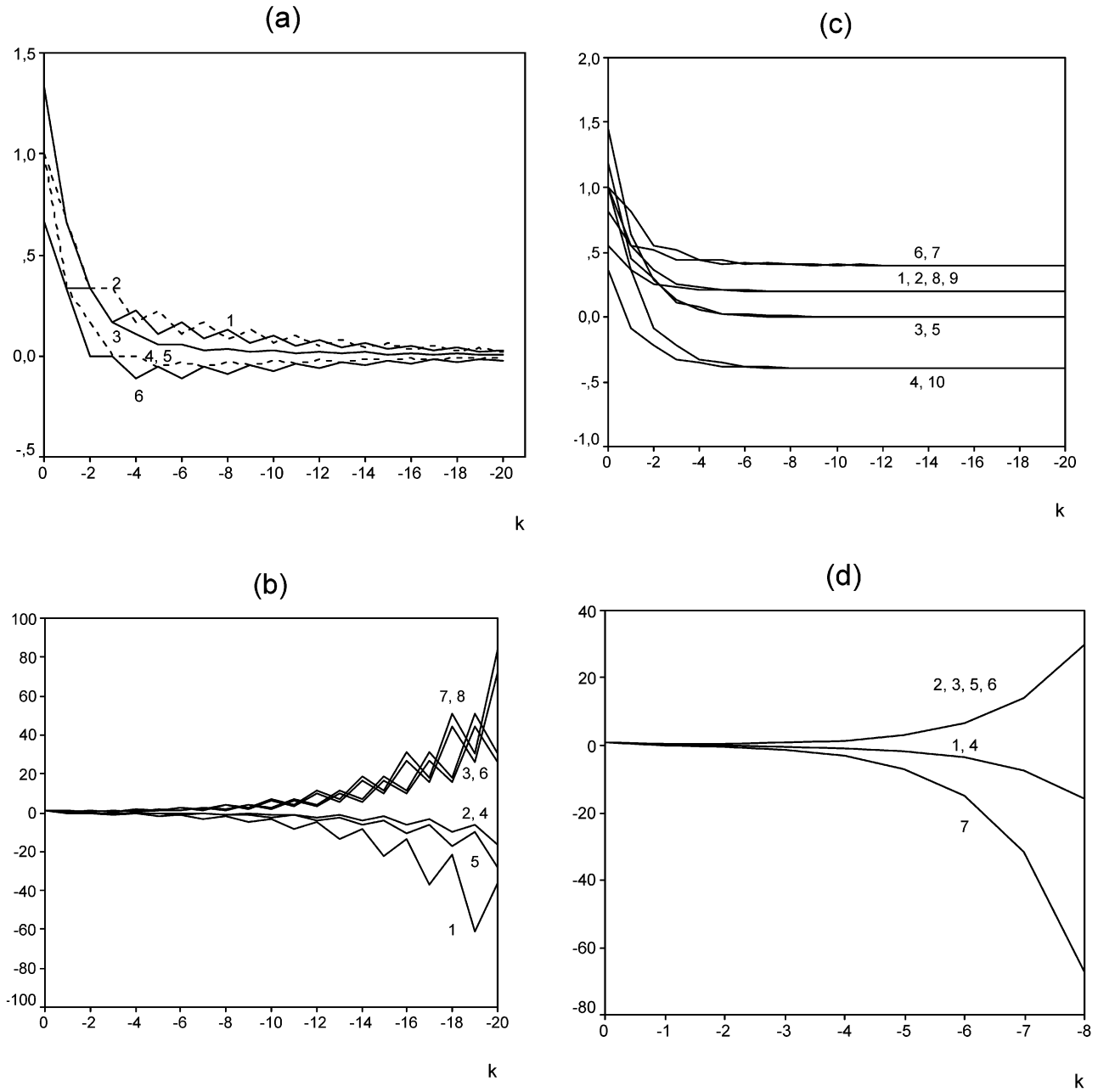

Figure 2. Atomic walk counts of negative order *k* plotted vs *k*. Numbers in the plot are vertex numbers as given in Figure 1: (a) ethylcyclobutane; (b) propyl-3-methylcyclobutane; (c) 4-methyl-3-ethylheptane; and (d) both bicyclo[2.2.1]heptane and dicyclopropylmethane.

those eigenvalues $\lambda_j \neq 0$ whose absolute value, denoted λ_0, is the smallest among all nonzero eigenvalues with the additional condition that $s_j^2 > 0$.[16] There may be more than one such λ_j, and among these there may be positive and negative ones.

There are three cases which have to be distinguished, corresponding to whether $\lambda_0 > 1$, $\lambda_0 = 1$, or $\lambda_0 < 1$ holds. Table 2 gives an overview.

If $\lambda_0 > 1$, then all summands in eq 17 eventually vanish as k approaches infinity, so that $||\mathbf{a}_{-k}|| \rightarrow 0$ for $k \rightarrow \infty$. Thus, in this case all walk counts of negative order converge to zero. Table 2 (top) lists four examples taken from ref 8, the graphs of ethylcyclobutane (Figure 1a), cyclopentane (a cyclic regular graph), 2-methylpropane (a star graph), and *n*-pentane (a short chain of odd length).

If $\lambda_0 = 1$, then all terms with $|\lambda_j| = 1$ are independent of k and have values s_j^2. The limit of $||\mathbf{a}_{-k}||^2$ for $k \rightarrow \infty$ then is their sum. Because by definition $s_j^2 > 0$ holds for all j with $|\lambda_j| = \lambda_0$, the limit of the sequence $||\mathbf{a}_{-k}||$ for $k \rightarrow \infty$ is nonzero. This case is represented by the graphs of 2,3-dimethylbutane (Table 2, middle) and 4-methyl-3-ethylheptane (Figure 1c,d and Table 2, middle). Such a case was not mentioned in ref 8.

The last case is $\lambda_0 < 1$. For any j with $|\lambda_j| = \lambda_0$, again $s_j^2 > 0$ holds by definition, and therefore $s_j^2 \lambda_j^{-2k} \rightarrow \infty$ for $k \rightarrow \infty$. Thus in this case $||\mathbf{a}_{-k}|| \rightarrow \infty$ for $k \rightarrow \infty$. Table 2 (bottom) lists four examples taken from ref 8, the graphs of *n*-butane (a short chain of even length), dicyclopropylmethane (Figure 1f), bicyclo[2.2.1]heptane (Figure 1e), and propyl-3-methylcyclobutane (Figure 1b).

Inspection of Table 1 suggests that the awc_{-k} values for a pair of vertices i and j approach some constant ratio for $k \rightarrow \infty$. Therefore, we now consider the normalized vectors $\mathbf{a}_{-k}/||\mathbf{a}_{-k}||$ and discuss their behavior ("direction") for $k \rightarrow \infty$. Our method results immediately from the observation that for negative order k and $k \rightarrow \infty$ the eigenvalues λ_j with $|\lambda_j| = \lambda_0$, as defined above, play the most important role. This is in full analogy to the important role of the largest eigenvalue λ_1 for positive order k.[1,10−12]

We have

$$\frac{\mathbf{a}_{-k}}{||\mathbf{a}_{-k}||} = \frac{\sum_{j\in J} s_j \lambda_j^{-k} \mathbf{x}_j}{\left(\sum_{j\in J} s_j^2 \lambda_j^{-2k}\right)^{0.5}} \qquad (18)$$

and multiplying the numerator and denominator of this quotient with λ_0^k we obtain

$$\frac{\mathbf{a}_{-k}}{||\mathbf{a}_{-k}||} = \frac{\sum_{j\in J} s_j (\lambda_0/\lambda_j)^k \mathbf{x}_j}{\left(\sum_{j\in J} s_j^2 (\lambda_0/\lambda_j)^{2k}\right)^{0.5}} \qquad (19)$$

For $k \rightarrow \infty$ all terms with $|\lambda_j| \neq \lambda_0$ approach zero, leaving the terms with $\lambda_0/\lambda_j = \pm 1$.

Therefore the denominator converges to $(\sum_{j\in J \text{ with } |\lambda_j|=\lambda_0} s_j^2)^{0.5}$, while the numerator eventually approaches some linear combination of eigenvectors $\mathbf{x}_j$ belonging to eigenvalues with absolute value λ_0. There is not necessarily a uniquely determined limit. In the following, we discuss some cases and examples. Again, Table 2 provides an overview.

If some λ_j with $|\lambda_j| = \lambda_0$ is negative or λ_0 appears with both signs, there are two sequences, one for odd and another for even k. The limits then are not necessarily eigenvectors of **A** themselves, but linear combinations of eigenvectors belonging to these different eigenvalues. This is the case for the bipartite examples of the case $\lambda_0 > 1$ (that is, all graphs except cyclopentane), see Table 1a and Figure 2a (ethylcyclobutane). This is also true for propyl-3-methylcyclobutane (Figure 2b), where the length of the unnormalized vectors grows to infinity. In the cases of *n*-butane or 2,3-dimethylbutane, there is only one eigenvalue λ_j with $|\lambda_j| = \lambda_0$, having negative sign), and therefore both odd and even sequences ($\mathbf{a}_{-k}/||\mathbf{a}_{-k}||$) converge against the same eigenvector of **A** except for the different sign.

If all λ_j are positive (simple or degenerate), the limit is uniquely determinated. This is true for cyclopentane, bicyclo-[2.2.1]heptane, and dicyclopropylmethane (Table 1c, Figures 1e,f and 2d), where the sequences belonging to the latter two graphs are identical. Another example is 4-methyl-3-ethylheptane (Figures 1c and 2c), where $\lambda_0 = 1$ appears as degenerate (double) eigenvalue. Table 1b shows the first 15 iterations with convergence to the vector (0.2, 0.2, 0, −0.4, 0, 0.4, 0.4, 0.2, 0.2, −0.4). It is easily seen (Figure 1d) that this vector is an eigenvector of **A** belonging to eigenvalue 1, that is, it is invariant under the Morgan algorithm.

For regular graphs, $\lambda_0 = \lambda_1$ holds, because all s_j are zero except for $j = 1$. Therefore the normalized vector sequence is constant and equal to **1**, which is the principal eigenvector. (This is also true for the "positive" direction, walking forward.) The graph of cyclopentane serves as an example.

For stars, $\lambda_0 = \lambda_1 = |\lambda_n|$ holds, because all s_j are zero except for $j = 1$ and $j = n$. The sequence is alternating.

For chains with an even number of vertices $n \geq 4$, there always exists an eigenvalue λ_j within the interval (−1, +1) with $s_j > 0$, so that $||\mathbf{a}_{-k}|| \rightarrow \infty$ holds and $\mathbf{a}_{-k}/||\mathbf{a}_{-k}||$ is alternating. For the graph of *n*-butane, the elements of the vectors $\mathbf{a}_{-k}$ are Fibonacci numbers.

For some short chains with odd number of vertices (n = 1, 5, 9) there are no eigenvalues with $s_j > 0$ in the interval (−1, +1). For these $||\mathbf{a}_{-k}|| \rightarrow 0$ holds.

CONCLUSION

The vectors of atomic walk counts, $\mathbf{a}_k$, are now easily calculated for both positive and negative orders k. Their limit behavior is determined for $k \rightarrow +\infty$ by the numerically largest eigenvalue λ_1, for $k \rightarrow -\infty$ by the numerically smallest eigenvalue λ_0 (under some provisos in both cases), such that for k moving from $-\infty$ to $+\infty$ the vector $\mathbf{a}_k$ after normalization gradually changes from an eigenvector corresponding to λ_0 to an eigenvector corresponding to λ_1 (or from/to a combination of such eigenvectors).

Both we[3,4] and others[17] used walk counts of positive order as descriptors not only for simple graphs corresponding to saturated hydrocarbon molecules but also for graphs containing multiple lines and loops corresponding to unsaturated and heteroatom-containing molecules. Adjacency matrices of such molecular graphs are still symmetric and as such amenable to the mathematical treatment given here.

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(13) If the eigenvalue λ_i is degenerate, definition (2) is ambiguous (except for the sign of s_i). In this case, the eigenvectors are not uniquely determined, but the sum of s_i^2 over the indices i belonging to the same eigenspace is uniquely determined, see ref 10.
(14) *Proof of the inclusion*. If there exists $\mathbf{y} \in \mathbf{A}^{-k}(\mathbf{a}_1)$ with $\mathbf{Ay} = \mathbf{z}$, then $\mathbf{A}^{k-1}(\mathbf{z}) = \mathbf{A}^k(\mathbf{y}) = \mathbf{a}_1$ and thus $\mathbf{z} \in \mathbf{A}^{-(k-1)}(\mathbf{a}_1)$.
(15) This is also true in the case of degenerate eigenvalues, as can be shown.
(16) Harary and Schwenk[9] define the main part of the spectrum, M, as those distinct eigenvalues with $s_j^2 > 0$. So, λ_0 is the smallest absolute value of a nonnull element of M.
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