

Relative Atomic Moments as Squared Principal Eigenvector Coefficients

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A proof is presented that the limit of each relative atomic moment (RAM) in tight-binding approximation is equal to the respective squared atomic coefficient in the principal eigenvector. It is also proved that this limit is reached when each higher RAM is obtained from the preceding one by multiplying by the squared largest eigenvalue. Relationships are obtained between the RAM limit and Ruckers' limit of the relative walk counts. Higher molecular branching and cyclicity as well as higher symmetry are shown to favor the convergence. The necessary and sufficient conditions are formulated for a RAM to reach its limit as early as in the second moment. Relationships between different RAMs are obtained for several classes of molecules

INTRODUCTION

During the last decade, self-returning walks in graphs attracted much attention due to their importance in the topological control of stability of molecules and crystals^{1–5} and that of chemical reactivity.^{6,7} They are closely related to the problems of isospectral and endospectral molecules and atoms,^{8–12} graph center,¹³ molecular branching, and cyclicity,^{14,15} etc.

In 1990, being on a sabbatical with L. B. Kier at Virginia Commonwealth University in Richmond, one of us (D.B.) performed a study of the relative atomic moments *RAM* (relative atomic self-returning walks). It was shown by many examples that RAMs are numerically equal to the squared coefficients of the principal eigenvector and, therefore, may be regarded as fractional electronic charges.¹⁶ The properties of these new atomic descriptors were studied, and, in a subsequent paper,¹⁷ they showed high correlation with the charges of 33 nonequivalent atoms in C₃–C₆ alkanes, obtained by the quantum chemical CNDO/2 method. In the last paper,¹⁷ a similar descriptor, called *NEC* (an abbreviation for normalized extended connectivities), was used and defined as the limit of the ratio of atomic and molecular extended connectivities. The proof of this limit and its analysis was left to be done in a subsequent paper. Unfortunately, for many reasons, the two papers^{16,17} were published after some delay and in reversed order in 1993 and 1992, respectively, and the results concerning the relative or normalized extended connectivities remained unpublished until now.

In the meantime, Rücker and Rücker¹⁸ proved, what Razinger¹⁹ had found earlier empirically, that Morgan's extended connectivities²⁰ are identical to the total number of walks of length *k* (atomic walk counts, *awc^k*), computed as row sums of the *k*th power of the adjacency matrix. Figueras²¹ shed some more light on the algorithm for computing *awc^k*s. In a subsequent paper, Rücker and Rücker derived formulas and presented analysis for the limit of the

relative extended connectivities.²² In this interesting and important paper there is a criticism of our 1992 paper: "Bonchev and Kier tacitly and erroneously assumed the existence of a limit distribution of vertices in simple trees which are typical examples of our second case". This criticism erroneously (though unfortunately not tacitly) assumed that we were unaware of more than a single distribution for simple trees.

It takes little time to find out that in acyclic molecules the extended connectivities oscillate and only rarely converge to a common limit. Thus, one necessarily deals with **two** limits, those for even and odd powers. We include here also the cases in which the limit is reached as early as in the second order connectivities (we used this terminology in our analysis¹⁶ of the limits for SRWs). In the 11 C₃–C₆ alkane molecules handled in our correlation¹⁷ only three had a single limit. It is transparent that we cannot include an oscillating variable in a correlation. Therefore, in inspecting our earlier paper, one might have asked which one of the two limits was actually used. The answer may appear somewhat surprising, but it has both theoretical justification and produced a higher correlation. We discarded that limit which made equivalent two or more nonequivalent atoms or made less difference between primary, secondary, tertiary and quaternary atoms. For six of the molecules that was the odd limit, and in the other two that was the even one.

For us, the moral of this story is straightforward. One should not publish a very laconic discussion of an idea for a future paper without a full discussion on the methodology. This not only caused problems of the type discussed above, but, as it turns out, others could prove to be faster. But, as the proverb says: "There is no bad, without good"; Ruckers' paper was partly stimulated by our earlier work, and, in turn, it has prompted us to present here the proof for the limit of RAMs, its properties, and its relations to the respective limit for the relative extended connectivities.

DERIVATION OF THE LIMIT FOR RELATIVE ATOMIC MOMENTS

Let $\lambda_1, \lambda_2, \dots, \lambda_n$ be eigenvalues of graph *G*, and **A** be its adjacency matrix. Since **A** is symmetric with respect to the main diagonal, an orthonormal basis **C**₁, **C**₂, ..., **C**_{*n*} of

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corresponding eigenvectors exists with c_{ji} being the i th coefficient of C_j . Denote the total number of self-returning walks of length k in G by $\text{SRW}^k(G)$, and denote those starting and ending at vertex i by SRW_i^k . As well known,¹⁻⁵ the graph-invariants SRW_i^k and $\text{SRW}^k(G)$ are measures for the atomic and molecular moments, μ_i^k and μ^k , respectively:

$$\mu_i^k = \text{SRW}_i^k \beta^k; \quad \mu^k(G) = \text{SRW}^k(G) \beta^n \quad (1)$$

where β is the resonance integral $H_{ja,jb}$ which, within the tight-binding approximation, weighs equally each one-step walk between the overlapping orbitals ja and jb of the neighboring atoms a and b in conjugated network of atoms. The equal weights of the SRWs make all of their ratios, that we deal with in this paper, valid for the ratios of the respective atomic moments, as well.

In a recent paper,¹⁶ Bonchev, Kier, and Mekenyan introduced the relative atomic moments $\mu_i^k/\mu^k(G)$ and found empirically (by calculating up to $k = 100$) that these ratios converge to a limit equal to the square of the respective coefficient in the principal eigenvector (lowest occupied molecular orbital, LOMO):

$$f_i = \lim_{k \rightarrow \infty} \mu_i^k / \mu^k(G) = \lim_{k \rightarrow \infty} \text{SRW}_i^k / \text{SRW}^k(G) = c_{1i}^2 \quad (2)$$

It is known that the k^{th} moment of energy can be presented as a sum of the k^{th} power eigenvalues:

$$\text{SRW}^k(G) = \sum_{j=1}^n \lambda_j^k \quad (3)$$

By multiplying (3) by the normalization condition

$$\sum_{i=1}^n c_{ji}^2 = 1 \quad (4)$$

one obtains

$$\text{SRW}^k(G) = \sum_{j=1}^n \lambda_j^k \sum_{i=1}^n c_{ji}^2 = \sum_{i=1}^n \sum_{j=1}^n \lambda_j^k c_{ji}^2 = \sum_{i=1}^n \text{SRW}_i^k \quad (5)$$

wherefrom a formula for the i^{th} atomic moments follows:

$$\text{SRW}_i^k = \sum_{j=1}^n \lambda_j^k c_{ji}^2 \quad (6)$$

From (6) and (3) one can find the limit for the relative atomic moments:

$$\lim_{k \rightarrow \infty} \frac{\text{SRW}_i^k}{\text{SRW}^k(G)} = \lim_{k \rightarrow \infty} \frac{\sum_{j=1}^n \lambda_j^k c_{ji}^2}{\sum_{j=1}^n \lambda_j^k} \quad (7)$$

Two cases must be considered:

(i) Nonalternant molecules (simple connected graphs)

In this case, $\lambda_1 > \lambda_j$ for any $j \neq 1$ and $\lambda_1^k \gg \lambda_j^k$ for $k \rightarrow \infty$. Hence,

$$f_i = (\lambda_1^k c_{1i}^2) / \lambda_1^k = c_{1i}^2 \quad (8)$$

(ii) Alternant molecules (bipartite graphs)

In this case, $\lambda_1 = |\lambda_n|$, $c_{1i}^2 = c_{ni}^2$, $k = \text{even}$ ($\mu^{\text{odd}} = 0$), and again

$$f_i = (\lambda_1^k c_{1i}^2 + \lambda_n^k c_{ni}^2) / (\lambda_1^k + \lambda_n^k) = c_{1i}^2 \quad (9)$$

We have thus proved within the tight-binding approximation that for any molecule or solid

$$f_i = \lim_{k \rightarrow \infty} \text{SRW}_i^k / \text{SRW}^k(G) = \lim_{k \rightarrow \infty} \mu_i^k / \mu^k(G) = c_{1i}^2 \quad (10)$$

Therefore, the relative atomic moments are equal to the partial atomic charges of the lowest unoccupied molecular orbital (LOMO) in a Hückel-type approximation, or, otherwise, they express the one-electron distribution over the atoms that correspond to the largest eigenvalue of adjacency matrix of the molecular graph. A plausible physical explanation of this result is that each self-returning walk (SRW_i^k) in the molecular graph is associated with an electron motion near the nucleus i and that the relative atomic moments are actually the relative frequencies of these electron motions. Such an interpretation is reminiscent of Feynman's ideas of accounting for all possible electron paths.²³

RELATIONSHIPS BETWEEN THE LIMITS FOR THE RELATIVE ATOMIC MOMENTS AND THOSE FOR THE RELATIVE ATOMIC WALK COUNTS (RELATIVE EXTENDED CONNECTIVITIES)

It was of interest to compare the limit found here for the relative atomic moments with that derived by Rucker and Rucker²² for the ratio between atomic and molecular walk counts (awc_i^k and mwc^k , respectively, where k is the walk length). The latter are important graph-invariants¹⁸ defined by the k^{th} power of the adjacency matrix:

$$\text{awc}_i^k = \sum_{j=1}^n a_{ji}^k \quad (11)$$

$$\text{mwc}^k = \sum_{i=1}^n \text{awc}_i^k = \sum_{i=1}^n \sum_{j=1}^n a_{ji}^k = a^k \quad (12)$$

The ratio of (11) and (12) defines the relative atomic walk count

$$p_i^k = \text{awc}_i^k / \text{mwc}^k \quad (13)$$

Rucker and Rucker²² derived the following limits for p_i :

(i) For $\lambda_1 > |\lambda_n|$ (nonalternant molecules)

$$p = \lim_{k \rightarrow \infty} p_i^k = c_{1i} / s_1 \quad (14)$$

where s_1 is the sum of all coefficients of c_1 .

Hence, by dividing (10) and (14) one obtains

$$f_i / p_i = c_{1i} s_1 \quad (15)$$

(ii) For $\lambda_1 = |\lambda_n|$ (alternant molecules)

(a) $k = \text{odd}$, $f_i = 0$, and $f_i / p_i = 0$

(b) $k = \text{even}$. By dividing (10) by formula (3b) of Rucker and Rucker²² one obtains

$$\frac{f_i^{\text{even}}}{p_i^{\text{even}}} = \frac{c_{1i}^2(s_1^2 + s_n^2)}{c_{1i}s_1 + c_{ni}s_n} \quad (16)$$

In case of $s_n = 0$, (16) reduces to (15).

It is known that awc^k 's increase faster with the walk length k than do SRW^k 's, and indeed this is true for mwc^k and SRW^k , respectively. Proceeding from eq 3 and R  cker and R  cker's equation²²

$$\text{mwc}^k = \sum_{j=1}^n \lambda_j^k s_j^2 \quad (17)$$

in which s_j is the sum of all coefficients of the eigenvector c_j , one can find that the ratio of the number of self-returning walks and the total number of walks has also a limit at high walk lengths k :

$$\lim_{k \rightarrow \infty} (\text{mwc}^k / \text{SRW}^k) = s_1^2 \quad (18)$$

From eqs 6, 15, 16, and 18 one finds the respective limit for the ratio of the two kinds of atomic walks:

(a) nonalternant molecules

$$\lim_{k \rightarrow \infty} (\text{SRW}_i^k / \text{awc}_i^k) = c_{1i} / s_1 \quad (19)$$

We have thus obtained what R  cker and R  cker²² called the normalized principal eigenvector coefficient and found it to be the limit of the relative atomic walk counts (eq 14).

(b) alternant molecules

$$\lim_{k \rightarrow \infty} \frac{\text{SRW}_i^k}{\text{awc}_i^k} = \frac{c_{1i}^2(s_1^2 + s_n^2)}{s_1^2(c_{1i}s_1 + c_{ni}s_n)} \quad (20)$$

For the specific case $s_n = 0$, eq 20 reduces to (19).

ANALYSIS OF THE CONVERGENCE OF ATOMIC AND MOLECULAR MOMENTS

Denote by $k_{\text{max}} = m$ the value of k at which our basic eq 2 holds within a prescribed accuracy. The following holds:

The limit of the relative atomic moments is reached when the ratio of any atomic $(m + 2)$ th and m th moment as well as the ratio of the $(m + 2)$ th and m th molecular moment becomes equal (within the prescribed accuracy) to the squared largest eigenvalue λ_1

$$\frac{\text{SRW}_i^{m+2}}{\text{SRW}_i^m} = \frac{\text{SRW}^{m+2}}{\text{SRW}^m} = \lambda_1^2 \quad (21)$$

Here, for brevity, we make use of the $(m + 2)$ th moments only because for alternant molecules the odd moments are zero. However, for nonalternant molecules the $(m + 1)$ th moments are actually used.

From eq 3 and the adjacency matrix properties one finds

$$\text{SRW}^2 \times \mathbf{A}^{m-2} = \text{SRW}^m = \sum \lambda_i^m$$

$$\text{SRW}^2 \times \mathbf{A}^m = \text{SRW}^{m+2} = \sum \lambda_i^{m+2}$$

wherefrom

$$\frac{\text{SRW}^{m+2}}{\text{SRW}^m} = \frac{\lambda_1^{m+2}}{\lambda_1^m} = \lambda_1^2 \quad (22)$$

The argument for the SRW_i s is analogous.

Our calculations have shown that k_{max} varies considerably, depending on the size of molecules and their topology. In some molecules k_{max} (determined with four decimal places accuracy for f_i) is higher than 100, in others it is less than 20, and even in some specific cases, which will be analyzed in the next section, $k_{\text{max}} = k_{\text{min}} = 2$. Generally, the speed of convergence depends on the factors that influence the approximate formula for the k th moment

$$\lim_{k \rightarrow \infty} \text{SRW}^k = \lim_{k \rightarrow \infty} \sum \lambda_i^k \approx \lambda_1^k \quad (23)$$

The larger the gap between λ_1 and the other eigenvalues, the lower the k value that would satisfy eq (23) within a given accuracy. In a good approximation, the gap of importance is $\Delta\lambda = \lambda_1 - \lambda_2$ for alternant molecules, and $\Delta\lambda = \lambda_1 - |\lambda_n|$ for nonalternant ones.

Evidently, the larger the molecule, the smaller the $\Delta\lambda$ gap, and the slower the convergence. Therefore, it was of greater interest to discuss the convergence in isomeric molecules. In Table 1, we compared C_6 and C_7 isomeric cross-conjugated polyenes. As seen in this table, the more branched molecules^{14,15} (those having more branches, or more central branches, or longer branches, etc.) have a larger $\lambda_1 - \lambda_2$ gap and converge faster. The higher symmetry could be an additional favorable factor when it produces higher degenerate λ_2 (or lower degenerate λ_n). This is, for example, the case of 3-ethylidene-1,4-pentadiene **10** which has a higher, doubly degenerate λ_2 eigenvalue.

Table 2 present data for the convergence in conjugated cyclic C_6 isomers, alternant (**11–22**), as well as nonalternant ones (**23–27**). The table illustrates the much slower convergence of nonalternant molecules, as compared to their alternant isomers from both Tables 1 and 2. The lower symmetry of the nonalternants eliminates the equality between λ_1 and $|\lambda_n|$, but $|\lambda_n|$ remains closer in value to λ_1 than do λ_2 . On the other hand, the higher symmetry frequently produces eigenvalue degeneracies; hence higher $\lambda_1 - \lambda_2$ or $\lambda_1 - |\lambda_n|$ and faster convergence. An example illustrating this point is provided by isomers **13** and **15** which differ only by the position of their single branch. The higher symmetry of **15** results in two degenerate eigenvalues which increases $\Delta\lambda$ from 0.403 to 0.562 and reduces k_{max} from 51 to 43.

The presence of more branches and/or more cycles in molecular skeleton, as major factors of molecular topology, also favors the convergence. The influence of molecular branching is well illustrated, for example, by the comparison of the three branched cyclopropene isomers **14**, **16**, and **22**, the increase in the number of branches in which decreases the convergence limit from $K = 43$ to 34 to 20, respectively. Other examples are the pairs of isomers **20** and **21** as well as **23** and **24**. Molecular cyclicity appears as a stronger factor than branching. Thus, the presence of a second atomic ring in **18** as compared to **12** reduces k_{max} from 50 to 27; similarly, the third atomic ring in **19** decreases the convergence limit from 32 to 26. Other examples can be found in Table 2. The monocyclic benzene molecule **27** with $k_{\text{max}} = 2$ does not violate this trend. It is a representative of a special class

Table 1. Convergence Limits of Isomeric C₆ and C₇ Cross-Conjugated Polyenes, Their Largest Eigenvalue and the Gap Between the Two Largest Eigenvalues

No	Molecular Graphs	λ_1	$\lambda_1 - \lambda_2$	k_{\max}^*
1		1.802	0.555	28
2		1.902	0.727	18
3		1.932	0.332	16
4		2.0	1.0	14
5		1.848	0.434	36
6		1.932	0.434	32
7		1.970	0.518	26
8		2.0	0.684	26
9		2.0	0.586	14
10		2.053	0.844	20

* k_{\max} is determined at the value of k at which for any atom i $SRW_i^k/SRW^k = SRW_i^{k+2}/SRW^{k+2}$ for the first four decimal places.

of molecules that does not change their atomic moments. They are discussed in detail in the next section.

ATOMS WITH CONSTANT RELATIVE ATOMIC MOMENTS

As found in our previous study,¹⁶ in some relatively rare cases the k th relative atomic moment (RAM) of certain atom i has a constant value for any $k \geq 2$:

$$f_i^k = \frac{\mu_i^k}{\mu^k} = \frac{\mu_i^2}{\mu^2} = \frac{a_i}{2E} \quad (24)$$

where a_i is the degree of vertex i and E is the number of graph edges.

The necessary and sufficient condition for the validity of eq 24 is the existence of relationships between all RAMs which allows one to write μ^k as a multiple of μ_i^k . If

$$\mu^k = \sum \mu_i^k = b\mu_i^k \quad (25)$$

holds for any $k \geq 2$, then

$$\frac{\mu_i^k}{\mu^k} = \frac{a_i}{2E} = \frac{1}{b}, \quad b = \frac{2E}{a_i} \quad (26)$$

The existence of (25) in alternant molecules is related to the equality of the sum of the moments of all starred (*) and all unstarred (#) atoms, proved in our parallel study:⁷

$$\sum_{i(*)} \mu_i^k = \sum_{i(\#)} \mu_i^k = \mu/2 \quad (27)$$

The simplest cases illustrating eq 24 are those described by star-graphs. The latter contain one central vertex c and several equivalent terminal vertices t adjacent to the central one.

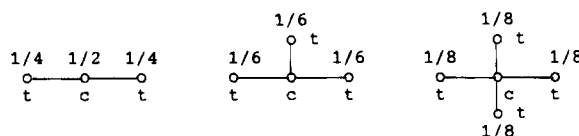


Table 2. Convergence Limits of Conjugated Cyclic C₆ Isomers, Their Largest Eigenvalue, and the Gap between the Two Largest Eigenvalues

No	Molecular graphs	λ_1	$\lambda_1 - \lambda_n $ ^a	k_{\max} ^b
11		2.115	0.254	75
12		2.278	0.387	50
13		2.539	0.403	51
14		2.228	0.454	43
15		2.562	0.562	43
16		2.334	0.594	34
17		2.438	0.682	32
18		2.414	0.682	27
19		2.732	0.732	26
20		2.655	0.789	28
21		2.709	0.806	26
22		2.414	1.414	20
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23		2.175	1.049	12
24		2.236	1.236	10
25		2.414	1.414	10
26		2.247	1.445	10
27		2	1	2

^a λ_2 is used instead of $|\lambda_n|$ for alternant molecules (#23–27). ^b k_{\max} is determined at the value of k at which for any atom i $SRW_i^k/SRW_i^k = SRW_i^{k+2}/SRW_i^{k+2}$ for the first four decimal places.

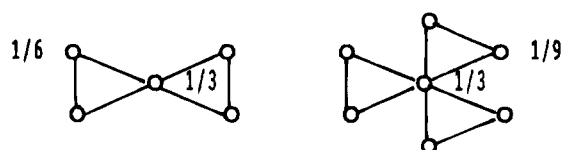
Here,

$$\sum \mu_{i(*)}^k = \mu_c^k = 1/2 \mu^k \quad (28)$$

$$\sum \mu_{i(\#)}^k = (n-1) \mu_t^k = E \mu_t^k = 1/2 \mu^k \quad (29)$$

and n and E are the total number of vertices and edges, respectively.

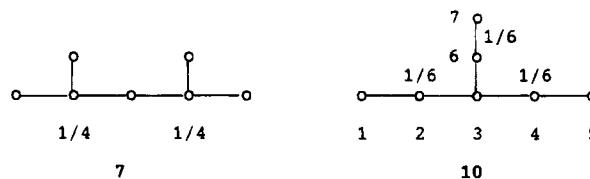
A similar vertex distribution exists in a class of graphs describing nonalternant structures with two or more spiro-connected trimembered rings



$$\mu_c^k = 1/3 \mu^k = (2/E) \mu^k; \quad \mu_t^k = \mu^k/E \quad (30)$$

Another simple case occurs when only the starred atoms are equivalent but the unstarred ones are not. Some examples

are shown below.



E.g., for 3-ethylidene-1,4-pentadiene **10** one obtains

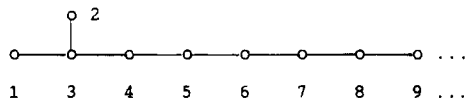
$$\mu_2^k + \mu_4^k + \mu_6^k = 3\mu_2^k = \mu^k/2 \quad (31)$$

wherefrom

$$\mu_2^k = \mu^k/6 \quad (32)$$

The above three classes of cases deal with simple molecules in which all atoms belonging to one of the two subsets of atoms are equivalent by symmetry. However, in more complicated molecules this is no longer possible. In such cases, eq (25) could remain valid only if in the subset

of starred atoms to which the i th atom belongs the sum of the moments of all atoms other than i must be a multiple of μ^k_i . 2-Methylene-polyenes are a convenient example.



Here,

$$\mu^k_1 = \mu^k_2 \quad (33)$$

$$\mu^k_4 + \mu^k_6 + \mu^k_8 + \dots = (n-3)\mu^k_1 \quad (34)$$

Hence,

$$\mu^k = 2(\mu^k_1 + \mu^k_2 + \mu^k_4 + \mu^k_6 + \dots) = 2E\mu^k_2 \quad (35)$$

Thus,

$$\mu^k_1 = \mu^k_2 = \mu^k/2E; \quad \mu^k_4 + \mu^k_6 + \mu^k_8 + \dots = \mu^k(n-3)/2E \quad (36)$$

In addition, for $C_{n=\text{odd}}$, the central atom $i = (n+3)/2$ of the longest chain has also a constant moment:

$$\mu^k_{(n+3)/2} = 2\mu^k_1 = \mu^k/E \quad (37)$$

Many examples of this class exist in cyclic alternant molecules and they frequently include the so-called isocodal or endospectral vertices.¹¹

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