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 relative extended connectivities. 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 analysis of the limits for SRWs). In the 11 C3-C6 alkane molecules handled in our correlation 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 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 $\lambda_1, \lambda_2, ..., \lambda_n$ 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...
corresponding eigenvectors exists with $c_{ji}$ being the $i$th coefficient of $C$. 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 $\text{SRW}^k_i$. As well known, the graph-invariants $\text{SRW}^k_i$ and $\text{SRW}^k(G)$ are measures for the atomic and molecular moments, $\mu^i$ and $\mu$, respectively:

$$\mu^i = \text{SRW}^k_i \beta^k; \quad \mu(G) = \text{SRW}^k(G) \beta^k$$

(1)

where $\beta$ 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, Bonchev, Kier, and Mekenyan introduced the relative atomic moments $\mu^i/\mu(G)$ 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):

$$f_i = \lim_{k \to \infty} \mu^i/\mu(G) = \lim_{k \to \infty} \text{SRW}^k_i/\text{SRW}^k(G) = \lambda^2_i$$

(2)

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

$$\text{SRW}^k(G) = \sum_{j=1}^{n} \lambda^k_j$$

(3)

By multiplying (3) by the normalization condition

$$\sum_{j=1}^{n} c^2_{ji} = 1$$

(4)

one obtains

$$\text{SRW}^k_i = \sum_{j=1}^{n} \lambda^k_j c^2_{ji}$$

(5)

wherefrom a formula for the $i$th atomic moments follows:

$$\text{SRW}^k_i = \sum_{j=1}^{n} \lambda^k_j c^2_{ji}$$

(6)

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

$$\lim_{k \to \infty} \frac{\text{SRW}^k_i}{\text{SRW}^k(G)} = \lim_{k \to \infty} \frac{\sum_{j=1}^{n} \lambda^k_j c^2_{ji}}{\sum_{j=1}^{n} \lambda^k_j}$$

(7)

Two cases must be considered:

(i) Nonalternant molecules (simple connected graphs)

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

$$f_i = (\lambda^k_1 c^2_1 - \lambda^k_l c^2_l)$$

(8)

(ii) Alternant molecules (bipartite graphs)

In this case, $\lambda_1 = |\lambda_l|$, $c^2_1 = c^2_l$, $k = \text{even}$ ($\mu^{\text{odd}} = 0$), and again

$$f_i = (\lambda^k_1 c^2_1 + \lambda^k_l c^2_l)(\lambda^k_1 + \lambda^k_l)$$

(9)

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

$$f_i = \lim_{k \to \infty} \text{SRW}^k_i/\text{SRW}^k(G) = \lim_{k \to \infty} \mu^i/\mu(G) = \lambda^2_i$$

(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$_i$) 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.

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 Rucker for the ratio between atomic and molecular walk counts (awc$_k$ and mwc$_k$, respectively, where $k$ is the walk length). The latter are important graph-invariants defined by the $k$th power of the adjacency matrix:

$$\text{awc}_k = \sum_{j=1}^{n} a^k_{ji}$$

(11)

$$\text{mwc}_k = \sum_{j=1}^{n} \text{awc}_j = \sum_{j=1}^{n} a^k_{ji}$$

(12)

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

$$p^k_i = \text{awc}_k/\text{mwc}^k$$

(13)

Rucker and Rucker derived the following limits for $p$:

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

$$p = \lim_{k \to \infty} p^k_i = c_i/s_1$$

(14)

where $s_1$ is the sum of all coefficients of $c_1$.

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

$$f/p_i = c_i/s_1$$

(15)

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

(a) $k = \text{odd}$, $f = 0$, and $f/p = 0$

(b) $k = \text{even}$. By dividing (10) by formula (3b) of Rucker and Rucker one obtains
In case of \( s_n = 0 \), (16) reduces to (15).

It is known that \( \text{awc}_k \) increases faster with the walk length \( k \) than do \( \text{SRW}_k \)'s, and indeed this is true for \( \text{mwc}_k \) and \( \text{SRW}_k \), respectively. Proceeding from eq 3 and Rucker and Rucker's equation(22):

\[
mwc^k = \sum_{j=1}^{n} \lambda_j^k s_j^2
\]

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 \( k \):

\[
\lim_{k \to \infty} \frac{\text{mwc}^k}{\text{SRW}^k} = s_1^2
\]

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

\[
\lim_{k \to \infty} \frac{\text{SRW}_k}{\text{awc}_k} = c_1/s_1
\]

We have thus obtained what Rucker and Rucker(22) called the normalized principal eigenvector coefficient and found it to be the limit of the relative atomic walk counts (eq 14).

(b) alternant molecules

\[
\lim_{k \to \infty} \frac{\text{SRW}_k}{\text{awc}_k} = \frac{c^2_1(s_1^2 + s_n^2)}{s_1^2(c_1 s_1 + c_n s_n)}
\]

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 molecule 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 \( \lambda_1 \):

\[
\frac{\text{SRW}^{m+2}}{\text{SRW}^m} = \frac{\lambda_1^{m+2}}{\lambda_1^m} = \lambda_1^2
\]

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

\[
\text{SRW}^2 \times A^{m-2} = \text{SRW}^m = \sum_{i} \lambda_i^m
\]

\[
\text{SRW}^2 \times A^{m} = \text{SRW}^{m+2} = \sum_{i} \lambda_i^{m+2}
\]

wherefrom

\[
\text{SRW}^{m+2}/\text{SRW}^m = \frac{\lambda_1^{m+2}}{\lambda_1^m} = \lambda_1^2
\]

The argument for the \( \text{SRW}_k \)'s is analogous.

Our calculations have shown that \( k_{\text{max}} \) varies considerably, depending on the size of molecules and their topology. In some molecules \( k_{\text{max}} \) (determined with four decimal places accuracy for \( f_j \)) 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

\[
\lim_{k \to \infty} \frac{\text{SRW}_k}{\text{awc}_k} = \lim_{k \to \infty} \lambda_i^k \approx \lambda_1^k
\]

The larger the gap between \( \lambda_1 \) 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 \( \Delta \lambda = \lambda_1 - \lambda_3 \) 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 \( \lambda_2 \) (or lower degenerate \( \lambda_3 \)). This is, for example, the case of 3-ethylidene-1,4-pentadiene 10 which has a higher, doubly degenerate \( \lambda_2 \) 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 \( \lambda_1 \) and \( \lambda_3 \), but \( \lambda_3 \) remains closer in value to \( \lambda_1 \) than do \( \lambda_2 \). On the other hand, the higher symmetry frequently produces eigenvalue degeneracies; hence higher \( \lambda_1 - \lambda_2 \) or \( \lambda_1 - \lambda_3 \) 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 \( k_{\text{max}} \) 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 cyclopropane 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 \( k_{\text{max}} \) 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 C\(_6\) and C\(_7\) Cross-Conjugated Polyenes. Their Largest Eigenvalue and the Gap Between the Two Largest Eigenvalues

<table>
<thead>
<tr>
<th>No</th>
<th>Molecular Graphs</th>
<th>(\lambda_1)</th>
<th>(\lambda_1 - \lambda_2)</th>
<th>(k_{\text{max}}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\circ) O O O O</td>
<td>1.802</td>
<td>0.555</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>(\circ) O O</td>
<td>1.902</td>
<td>0.727</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>(\circ) O O</td>
<td>1.932</td>
<td>0.332</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>(\circ) O O</td>
<td>2.0</td>
<td>1.0</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>(\circ) O O O O</td>
<td>1.848</td>
<td>0.434</td>
<td>36</td>
</tr>
<tr>
<td>6</td>
<td>(\circ) O O</td>
<td>1.932</td>
<td>0.434</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>(\circ) O O</td>
<td>1.970</td>
<td>0.518</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>(\circ) O O</td>
<td>2.0</td>
<td>0.684</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>(\circ) O O</td>
<td>2.0</td>
<td>0.586</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>(\circ) O O O O</td>
<td>2.053</td>
<td>0.844</td>
<td>20</td>
</tr>
</tbody>
</table>

* \(k_{\text{max}}^*\) is determined at the value of \(k\) at which for any atom \(i\) \(\text{SRW}_i^k/\text{SRW}_i^k = \text{SRW}_{i+1}^k/\text{SRW}_{i+2}^k\) 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 \(k \geq 2\):

\[
\mu_i^k = \frac{a_i}{\mu^2} = \frac{a_i}{2E}
\]

(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 \(\mu^k\) as a multiple of \(\mu_i^k\). If

\[
\mu^k = \sum \mu_i^k = b \mu_i^k
\]

holds for any \(k \geq 2\), then

\[
\frac{\mu_i^k}{\mu^k} = \frac{a_i}{2E} = \frac{1}{b^i} \quad b = \frac{2E}{a_i}
\]

(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

\[
\sum_{i(*)} \mu_i^k = \sum_{i(\#)} \mu_i^k = \mu/2
\]

(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 | \( \lambda_1 \)  | \( |\lambda_1| - |\lambda_1| \)  | \( k_{\text{III}} \) |
|----|------------------|-----------------|----------------|----------------|
| 11 | ![Molecular graphs](image) | 2.115 | 0.254 | 75 |
| 12 | ![Molecular graphs](image) | 2.278 | 0.387 | 50 |
| 13 | ![Molecular graphs](image) | 2.539 | 0.403 | 51 |
| 14 | ![Molecular graphs](image) | 2.228 | 0.454 | 43 |
| 15 | ![Molecular graphs](image) | 2.562 | 0.562 | 43 |
| 16 | ![Molecular graphs](image) | 2.334 | 0.594 | 34 |
| 17 | ![Molecular graphs](image) | 2.438 | 0.682 | 32 |
| 18 | ![Molecular graphs](image) | 2.414 | 0.682 | 27 |
| 19 | ![Molecular graphs](image) | 2.732 | 0.732 | 26 |
| 20 | ![Molecular graphs](image) | 2.655 | 0.789 | 28 |
| 21 | ![Molecular graphs](image) | 2.709 | 0.806 | 26 |
| 22 | ![Molecular graphs](image) | 2.414 | 1.414 | 20 |
| 23 | ![Molecular graphs](image) | 2.175 | 1.049 | 12 |
| 24 | ![Molecular graphs](image) | 2.236 | 1.236 | 10 |
| 25 | ![Molecular graphs](image) | 2.414 | 1.414 | 10 |
| 26 | ![Molecular graphs](image) | 2.247 | 1.445 | 10 |
| 27 | ![Molecular graphs](image) | 2 | 1 | 2 |

\( ^a \lambda_2 \) is used instead of \( |\lambda_n| \) for alternant molecules (#23–27). \( ^b k_{\text{max}} \) is determined at the value of \( k \) at which for any atom \( i \) SRW\(^k\)/SRW\(^{k+2}\) = SRW\(^{k+2}\)/SRW\(^{k+4}\) for the first four decimal places.

Here,

\[
\sum \mu^k_{(c)} = \mu^c = 1/2\mu^k \tag{28}
\]

\[
\sum \mu^k_{(c)} = (n - 1)\mu^c = E\mu^c = 1/2\mu^k \tag{29}
\]

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

![Molecular graphs](image)

\( \mu^c = 1/3 \mu^k = (2/E)\mu^k; \quad \mu^c = \mu^k/E \tag{30} \)

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

![Molecular graphs](image)

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

\[
\mu^k_2 + \mu^k_4 + \mu^k_6 = 3\mu^k_2 = \mu^k/2 \tag{31}
\]

wherefrom

\[
\mu^k_2 = \mu^k/6 \tag{32}
\]

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 is the sum of the moments of all atoms other than $i$ must be a multiple of $\mu^k$. 2-Methylene-polyenes are a convenient example.

\[ \mu_1^k = \mu_2^k \]  \hspace{1cm} (33)
\[ \mu_4^k + \mu_6^k + \mu_8^k + \ldots = (n-3)\mu_1^k \] \hspace{1cm} (34)

Hence,
\[ \mu^k = 2(\mu_1^k + \mu_2^k + \mu_4^k + \mu_6^k + \ldots) = 2E\mu_2^k \] \hspace{1cm} (35)

Thus,
\[ \mu_1^k = \frac{\mu_2^k}{2E}; \quad \mu_4^k + \mu_6^k + \mu_8^k + \ldots = \frac{\mu^k(n-3)}{2E} \] \hspace{1cm} (36)

In addition, for $C_{n=odd}$ the central atom $i = (n+3)/2$ of the longest chain has also a constant moment:
\[ \mu_{(n+3)/2}^k = 2\mu_1^k = \frac{\mu^k}{E} \] \hspace{1cm} (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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