Complementing the Proof of the Limit of Relative Atomic Moments

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A recent proof (*J. Chem. Inf. Comput. Sci.* **1995**, *35*, 237−242) that the limit of each relative atomic moment in tight binding approximation is equal to the respective squared atomic coefficient in the principal eigenvector is completed.

INTRODUCTION

Three of the present authors[1] provided recently a proof of a previously empirically observed regularity[2,3] concerning the relative atomic moments (RAMs). They, namely, showed that in the limit case when the length of the walks tend to infinity a RAM is equal to the square of the respective coefficient in the principal eigenvector (lowest occupied molecular orbital, LOMO). At a certain stage the proof[1] is incomplete, and the aim of this note is to fill this gap.

We adopt the same notation as used previously.[1] Thus the kth relative moment of the ith atom is defined as

$$\mathrm{RAM}^k{}_i = \mathrm{SRW}^k{}_i/\mathrm{SRW}^k \qquad (1)$$

where $\mathrm{SRW}^k = \mathrm{SRW}^k(G)$ is the number of self-returning walks of length k in the molecular graph G, and where $\mathrm{SRW}^k{}_i$ is the number of self-returning walks of length k, starting and ending at the ith vertex of G. As explained in ref 1, the definition (1) assumes the applicability of the tight-binding approximation in which one-step walks exist only between vertices corresponding to chemically bonded atoms and in which all one-step walks have equal weights. Now, by means of numerical examples it was found[2,3] that if k is sufficiently large, then $\mathrm{RAM}^k{}_i$ becomes equal to $(c_{1i})^2$, where c_{1i} is the coefficient on the ith vertex of the normalized principal eigenvector C_1 of the molecular graph G. This fact can be expressed as

$$f_i = \lim_{k\to\infty} \mathrm{SRW}^k{}_i/\mathrm{SRW}^k = (c_{1i})^2 \qquad (2)$$

provided that the respective limit exists. (Recall that C_1 is the eigenvector of G corresponding to the eigenvalue λ_1 which is the maximal eigenvalue of G. If G is a connected graph, then there are mathematical theorems[4] guaranteeing that all the coefficients c_{1i}, $i = 1,2,...,n$, are real and positive numbers.)

Formula (2) should be used with caution because the limit on its right-hand side does not necessarily exist. This limit always exists for nonbipartite graphs. In the case of bipartite graphs, however, SRW^k and $\mathrm{SRW}^k{}_i$ are zero whenever k is odd, and then the quotient $\mathrm{SRW}^k{}_i/\mathrm{SRW}^k$ is meaningless. Consequently, for bipartite graphs the limit on the right-hand side of (2) has to be taken over even values of k.

Following ref 1 we denote by $\lambda_1, \lambda_2, ..., \lambda_n$ the eigenvalues of the graph G and by $C_1, C_2, ..., C_n$ the respective orthonormal eigenvectors; c_{ji} is the ith coefficient of the jth eigenvector. Further, **A** is the adjacency matrix of G. Then the relations (3) and (4) hold

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

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

By combining (3) and (4) the authors of ref 1 arrived at

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

from which they concluded that formula (6) for the ith atomic moment can be obtained

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

Eventually (3) and (6) are substituted back into (2) and the limit f_i is calculated.[1] Notice that the present eqs 2−6 are numbered (2)−(6) also in ref 1.

Unfortunately, eq 6 does not necessarily follow from eq 5.

Therefore the proof of the main result of ref 1, namely of the validity of the limit (2), is incomplete. In the subsequent section we offer a remedy.

PROOF OF EQUATION 6

The eigenvalue-eigenvector equation of the adjacency matrix is

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$$\mathbf{A}C_j = \lambda_j C_j;\quad j = 1,2,...,n$$

which can be written in a more compact form as

$$\mathbf{A}C = C\Lambda \tag{7}$$

where $\mathbf{C} = (C_1,C_2,...,C_n)$ and $\Lambda = \mathrm{diag}[\lambda_1,\lambda_2,...,\lambda_n]$. The matrix $\mathbf{C}$ is unitary, namely it has the property $CC^\dagger = C^\dagger C = I$ = unit matrix of order n. (As usual, if $C = ||c_{ij}||$ then $C^\dagger = ||c_{ji}^*||$ with z^* symbolizing the complex conjugate of z.)

Multiplication of eq 7 from the left by $\mathbf{A}$ gives

$$\mathbf{A}^2C = \mathbf{A}(C\Lambda) = (\mathbf{A}C)\Lambda = (C\Lambda)\Lambda = C(\Lambda\Lambda) = C\Lambda^2$$

Continuing the same argument

$$\mathbf{A}^kC = \mathbf{C}\Lambda^k \tag{8}$$

for any $k = 2,3,....$ Multiplying $\mathbf{A}^kC$ from the right by $C^\dagger$ we have

$$(\mathbf{A}^kC)C^\dagger = \mathbf{A}^k(CC^\dagger) = \mathbf{A}^kI = \mathbf{A}^k$$

and therefore eq 8 yields

$$\mathbf{A}^k = C\Lambda^kC^\dagger \tag{9}$$

It is straightforward that $\Lambda^k = \mathrm{diag}[(\lambda_1)^k,(\lambda_2)^k,...,(\lambda_n)^k]$. In view of this, by performing the matrix multiplication on the right-hand side of (9) we obtain the formula

$$(\mathbf{A}^k)_{ij} = \sum_{h=1}^{n}(\lambda_h)^k c_{hi}c_{hj}^* \tag{10}$$

which gives the number of walks of length k between the vertices i and j. If the graph eigenvectors are chosen so that all their components are real-valued, $c_{hj}^* = c_{hj}$, then eq 6 is just the special case of (10) for $i = j$.

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