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Spectral moments of polymer graphs

Ivan Gutman[1], **Vladimir R. Rosenfeld**[2]
[1] Institute of Physical Chemistry, Attila Jozsef University, P.O. Box 105, H-6701 Szeged, Hungary; on leave from Faculty of Science, University of Kragujevac
[2] Department of Chemistry, Technion, Haifa 32000, Israel

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Summary. It is shown that for any k, the kth spectral moment of a polymer graph composed of n monomer units is an exact linear function of the parameter n. This linear relation holds for all values of n, greater than a critical value $\xi_0 = \xi_0(k)$.

Key words: Spectral moments – Molecular graph – Graph theory – Polymers

Introduction

If $\lambda_1, \lambda_2, \dots, \lambda_N$ are the eigenvalues of a molecular graph G, then the kth spectral moment of G is defined as

$$M_k = M_k(G) = \sum_{i=1}^{N} (\lambda_i)^k.$$

Since the pioneering works of Hall [1] and Marcus [2], graph spectral moments found numerous applications in quantum chemistry [1–14] and in solid-state physical chemistry [15–20], and their theory is nowadays well elaborated. Spectral moments are related to a special type of random walks (see below). There is a rich statistical-mechanical literature on random walks of graphs, especially, but not exclusively, of lattice graphs (see, for instance, Refs. [21–26] and the references cited therein).

A problem studied in considerable detail is the dependence of M_k on molecular structure [27–31]. This dependence was first investigated by Marcus [2], who put forward solutions for $k = 2, 4$ and 6. Eventually, the cases $k = 8$ [28, 30], $k = 10$ [29] and $k = 12$ [31] were resolved for benzenoid systems, but with increasing k the respective expressions become so complicated that much progress along these lines is hardly to be expected.

Another direction of research on spectral moments was recently initiated by proving [32] that the spectral moments of linear polyacenes with h hexagons are linear functions of h. This result could be obtained thanks to the fact that explicit analytical expressions are known for the eigenvalues of linear polyacenes. Since for the vast majority of polymer graphs no such expressions are known, the proof technique employed in Ref. [32] cannot be employed in the case of other classes of polymer graphs.

However, in the same work [32], by means of numerical examples, it was established that also in many other homologous series the spectral moments increase as (exact) linear functions of the number of building blocks. In fact, if n denotes the number of monomer units and X_n is the respective polymer graph, then the relation

$$M_k(X_n) = An - B \tag{1}$$

was empirically found to be satisfied in many cases; here A and B are parameters depending on the nature of the polymer examined as well as on k, but independent of n. Formula (1) is usually violated by the first few members of the homologous series. However, for n being greater than a critical value $\xi_0 = \xi_0(k)$, Eq. (1) is satisfied exactly.

In this paper we show that the above-described size dependency of the spectral moments is, indeed, a generally valid regularity.

Preliminary considerations

In this work we consider two types of polymer graphs, which we denote by G_n and g_n. Let G be an arbitrary graph and $x_1, x_2, \ldots, x_p, y_1, y_2, \ldots, y_p$ be its certain (not necessarily distinct) vertices.

The *class 1* polymer graph G_n, $n \geqslant 2$, is obtained by taking n copies of G and by joining (by means of a new edge) the vertex x_j of the ith copy with the vertex y_j of the $(i+1)$th copy, and by repeating this for $j = 1, 2, \ldots, p$ and $i = 1, 2, \ldots, n-1$. In addition to this, G_1 is chosen so as to be isomorphic with G.

The *class 2* polymer graph g_n, $n \geqslant 2$, is obtained by taking n copies of G and by identifying the vertex x_j of the ith copy with the vertex y_j of the $(i+1)$th copy, and by repeating this for $j = 1, 2, \ldots, p$ and $i = 1, 2, \ldots, n-1$. In addition to this, we define g_1 so as to coincide with G.

The vertex of g_n, obtained by identifying the vertex x_j of the ith copy of G with the vertex y_j of the $(i+1)$th copy of G, will be denoted by $z_{j,i}$, $i = 1, 2, \ldots, n-1$. To maintain consistency, we label the vertices, $x_1, x_2, \ldots, x_p$ of the first copy of G by $z_{1,0}, z_{2,0}, \ldots, z_{p,0}$, and the vertices $y_1, y_2, \ldots, y_p$ of the nth copy of G by $z_{1,n}, z_{2,n}, \ldots, z_{p,n}$.

Notice that if G has N vertices and M edges, then G_n has nN vertices and $nM + (n-1)p$ edges, whereas g_n possesses $nN - (n-1)p$ vertices and nM edges.

From the way in which the graphs G_n and g_n are constructed one immediately deduces the following.

Lemma 1. *Let $n \geqslant m \geqslant 1$. The polymer graphs G_n and g_n contain $n - m + 1$ distinct subgraphs isomorphic to G_m and g_m, respectively.*

A walk in a graph G is an ordered sequence $\mathbf{w} = (v_0, v_1, \ldots, v_k)$ of vertices of G, such that for $i = 1, \ldots, k$, the vertices v_{i-1} and v_i are adjacent. This walk is said to be of length k. (In statistical mechanics, especially when G represents a lattice, $\mathbf{w}$ is usually referred to as a "random walk" [21–24].) Note that it is not required that the vertices of $\mathbf{w}$ are all mutually different. If v_0 and v_k coincide, then $\mathbf{w}$ is said to be self-returning (or closed) walk.

An elementary result in the theory of spectral moments is

$$M_k(G) = \text{number of self-returning walks of length } k \text{ in } G. \tag{2}$$

Marcus [2] seems to be the first who explicitly stated and proved Eq. (2), although the result was certainly known also to earlier authors. Eventually, Eq. (2) was restated and reproven by many other researchers in this field.

In the case of polymer graphs G_n and g_n, a self-returning walk may involve vertices from several monomer units. In the case of class 1 polymer graphs G_n, we simply say that a self-returning walk **w** passes through a particular monomer unit of G_n if it contains at least one vertex of that monomer unit. The situation with the class 2 polymer graphs g_n is somewhat more complicated. A self-returning walk of **w** of g_n passes through the ith monomer unit of g_n if it contains at least two vertices of that unit which neither both belong to the set $\{z_{1,i-1}, z_{2,i-1}, \dots, z_{p,i-1}\}$ nor both belong to the set $\{z_{1,i}, z_{2,i}, \dots, z_{p,i}\}$.

We further say that **w** has extent ξ if it passes through ξ monomer units, but does not pass through $\xi+1$ monomer units.

The number of self-returning walks of G_n and g_n of length k and of extent ξ is denoted by $W_k(G_n, \xi)$ and $W_k(g_n, \xi)$, respectively.

Lemma 2. *Let G_n and g_n be polymer graphs of class 1 and 2, respectively, composed of n monomer units, $n \geqslant 1$. Then*

(a) $W_k(G_n, \xi) = (n-\xi+1)\, W_k(G_\xi, \xi)$ *if* $1 \leqslant \xi \leqslant n$,

$W_k(g_n, \xi) = (n-\xi+1)\, W_k(g_\xi, \xi)$ *if* $1 \leqslant \xi \leqslant n$,

(b) $W_k(G_n, \xi) = 0$, *if* $\xi > n$,

$W_k(g_n, \xi) = 0$ *if* $\xi > n$.

Proof. Part (b) of Lemma 2 is a straightforward consequences of the definition of the quantities $W_k(G_n, \xi)$ and $W_k(g_n, \xi)$. In order to verify part (a) notice that each self-returning walk of G_n or g_n of extent ξ is at the same time a self-returning walk of a unique subgraph of G_n or g_n, respectively, composed of ξ monomer units. By Lemma 1 the number of such subgraphs is $n-\xi+1$. □

Proving Eq. (1)

In order to arrive at Eq. (1), we must first observe that self-returning walks of length k may pass through only a limited number of monomer units of G_n or g_n. Denote by $\xi_0 = \xi_0(k)$ the greatest number of monomer units which a self-returning walk can embrace, i.e.

$$W_k(G_\xi, \xi) > 0 \quad \text{and} \quad W_k(g_\xi, \xi) > 0 \quad \text{for } \xi \leqslant \xi_0,$$
$$W_k(G_\xi, \xi) = 0 \quad \text{and} \quad W_k(g_\xi, \xi) = 0 \quad \text{for } \xi > \xi_0. \tag{3}$$

Consider first the polymer graphs of class 1 and examine their spectral moments $M_k(G_n)$. Then, in view of relations (2) and (3),

$$M_k(G_n) = \sum_{\xi=1}^{\infty} W_k(G_n, \xi) = \sum_{\xi=1}^{\xi_0} W_k(G_n, \xi). \tag{4}$$

We have now to distinguish between two cases

Case 1: $n \leqslant \xi_0$. Then by Lemma 2(b), Eq. (4) reduces to

$$M_k(G_n) = \sum_{\xi=1}^{n} W_k(G_n, \xi)$$

and by Lemma 2(a) we have

$$M_k(G_n) = \sum_{\xi=1}^{n} (n-\xi+1) W_k(G_\xi, \xi) = n \sum_{\xi=1}^{n} W_k(G_\xi, \xi) - \sum_{\xi=1}^{n} (\xi-1) W_k(G_\xi, \xi). \tag{5}$$

Both summations on the right-hand side of Eq. (5) depend on n and therefore the entire expression on the right-hand side of (5) is not a linear function of n.

Case 2: $n > \xi_0$. Bearing in mind Lemma 2(a), Eq. (4) yields

$$M_k(G_n) = \sum_{\xi=1}^{\xi_0} (n-\xi+1) W_k(G_\xi, \xi) = n \sum_{\xi=1}^{\xi_0} W_k(G_\xi, \xi) - \sum_{\xi=1}^{\xi_0} (\xi-1) W_k(G_\xi, \xi). \tag{6}$$

Both summations on the right-hand side of (6) are independent of the parameter n and, consequently, the kth spectral moment of G_k is a linear function of n.

The above conclusions can be summarized as follows

Theorem 1. *For any value of* k, $k > 0$, *an integer* $\xi_0 = \xi_0(k)$ *can be found, such that Eq.* (1) *holds for* $X_n = G_n$, $n > \xi_0$. *In other words, Eq.* (1) *holds for polymer graphs of class 1, provided the number of monomer units is sufficiently large. Furthermore, the coefficients A and B occurring in Eq.* (*1*) *are given by*

$$A = \sum_{\xi=1}^{\xi_0} W_k(G_\xi, \xi) \quad \text{and} \quad B = \sum_{\xi=1}^{\xi_0} (\xi-1) W_k(G_\xi, \xi).$$

The analysis of the spectral moments of polymer graphs of class 2 is similar, but somewhat more complicated. In this case, namely, the expression $\sum_{\xi=1}^{n} W_k(g_n, \xi)$ does not count all self-returning walks of g_n of length k. The walks omitted in the latter sum are those embracing only some of the vertices $z_{1,i}, z_{2,i}, \ldots, z_{p,i}$ for some fixed value of i, $0 \leqslant i \leqslant n$. For each value of i the number of such walks is the same. It is convenient to denote this number by $W_k(G_0, 0)$. Because there are $n+1$ distinct values of i, the total number of such walks is $(n+1) W_k(G_0, 0)$ which, in order to make our notation compact, we denote by $W_k(G_n, 0)$.

Instead of Eqs. (4)–(6) we now have

$$M_k(G_n) = \sum_{\xi=0}^{\infty} W_k(g_n, \xi) = \sum_{\xi=0}^{\xi_0} W_k(g_n, \xi)$$

$$M_k(G_n) = \sum_{\xi=0}^{n} (n-\xi+1) W_k(g_\xi, \xi) = n \sum_{\xi=0}^{n} W_k(g_\xi, \xi) - \sum_{\xi=0}^{n} (\xi-1) W_k(g_\xi, \xi) \quad \text{if } n \leqslant \xi_0$$

$$M_k(g_n) = \sum_{\xi=0}^{\xi_0} (n-\xi+1) W_k(g_\xi, \xi) = n \sum_{\xi=0}^{\xi_0} W_k(g_\xi, \xi) - \sum_{\xi=0}^{\xi_0} (\xi-1) W_k(g_\xi, \xi) \quad \text{if } n > \xi_0$$

and in full analogy with Theorem 1 we deduce:

Theorem 2. *For any value of k, $k > 0$, an integer $\xi_0 = \xi_0(k)$ can be found, such that Eq.* (1) *holds for $X_n = g_n$, $n > \xi_0$. In other words, Eq.* (1) *holds for polymer graphs of class 2, provided the number of monomer units is sufficiently large. Furthermore, the coefficients A and B occurring in Eq.* (1) *are given by*

$$A = \sum_{\xi=0}^{\xi_0} W_k(g_\xi, \xi) \quad \text{and} \quad B = \sum_{\xi=0}^{\xi_0} (\xi - 1) W_k(g_\xi, \xi).$$

Needless to say that ξ_0 in Theorems 1 and 2 have different values.

Discussion

In order to get a better insight into the result formulated in Theorems 1 and 2, we would need to know what "sufficiently large" means with regard to the number of monomer units. This information may also be important for any practical application of Eq. (1). The value of ξ_0 depends in a complicated way both on the structure of the monomer unit G and on the way in which the monomers are coupled together. Here we consider only the simplest case, namely when the shortest path going through a monomer unit starts at the vertex y_j and ends at vertex x_j.

Consider first polymer graphs of class 1. Let, as before, G be the molecular graph of the monomer unit. Let the distance between y_j and x_j in G be d. Then the shortest self-returning walk having extent ξ must be of length $k = (2d + 2) \xi - (4d + 2)$. Indeed, such a walk would start at the vertex x_j of a certain, say hth, monomer unit, continue to vertex y_j of the $(h + 1)$th monomer unit (one step), continue to vertex x_j of the $(h + 1)$th monomer unit (d steps), continue to vertex y_j of the $(h + 2)$th unit (one step), etc., arrive at vertex x_j of the $(h + \xi - 2)$th unit (d steps) and continue to vertex y_j of the $(h + \xi - 1)$th unit (one step), thus passing through ξ monomer units. This requires a total of $(\xi - 1) + (\xi - 2) d = (d + 1)\xi - (2d + 1)$ steps. The same number of steps is needed to return to the starting vertex.

Hence in this case ξ_0 and k are related as

$$(2d + 2)\xi_0 - (4d + 2) \leqslant k < (2d + 2)(\xi_0 + 1) - (4d + 2). \tag{7}$$

Setting $\xi_0 = 1$ into Eq. (7) we obtain $-2d \leqslant k < 2$ which means that $\xi_0(1) = 1$. Setting $\xi_0 = 2$ in Eq. (7) we obtain $2 \leqslant k < 2d + 4$ which implies $\xi_0(2) = \xi_0(3) = \cdots = \xi_0(2d + 3) = 2$, etc.

When calculating ξ_0, the case of polymer graphs of class 2 is simpler. Under the above-described conditions the shortest self-returning walk of g_n having extent ξ must be of length $k = 2[2 + (\xi - 2)d] = 2d\xi - (4d - 4)$. Instead of Eq. (7) we now have

$$2d\xi_0 - (4d - 4) \leqslant k < 2d(\xi_0 + 1) - (4d - 4)$$

from which one concludes $\xi_0(1) = \xi_0(2) = \xi_0(3) = 1$, $\xi_0(4) = \xi_0(5) = \cdots = \xi_0(2d + 3) = 2$, etc.

The result communicated in this paper has one obvious application. If one is interested in the kth spectral moments of a homologous series then it is sufficient to evaluate numerically this moment for only two members of the series. If the respective members are large enough, then Eq. (1) is applicable, the parameters A and B can readily be computed and thus all kth spectral moments (except, perhaps, the first few members of the series) become available. What is "large enough" can be estimated using the above-described procedure. The critical parameter $\xi_0(k)$, which determines when exact linearity begins, is a very slowly increasing function of k, thus making numerical calculations of the spectral moments quite easy.

Generalizations and extensions

Using reasoning analogous to, but sometimes somewhat more complex than what is outlined in the preceding sections, we arrive at the following generalizations and extensions of Theorems 1 and 2 [33]. We state them without proofs.

If the polymer graph considered is cyclic. i.e., if its terminal monomer units are joined together in the same manner as other monomer units, then we have

$$M_k(X_n) = An$$

with the same parameter A as in Eq. (1).

If the open-chain polymer graph has arbitrary terminal fragments (U and V), differing from the monomer units, then instead of Eq. (1) we have

$$M_k(X_n) = An - C$$

also with A the same as in Eq. (1). Furthermore, $C = C_U + C_V$, such that C_U is independent of V and C_V is independent of U.

If m copies of the polymer X_n are bound in an $m \times n$ rectangular network, $Y_{m,n}$, then for m and n being sufficiently large, the kth spectral moment of $Y_{m,n}$ is an exact linear function of m and an exact linear function of n, i.e.,

$$M_k(Y_{m,n}) = A'm + B'n + C'mn + D'$$

with A', B', C' and D' being independent of m and n. In the special case of a square $n \times n$ network,

$$M_k(Y_{n,n}) = A''n^2 + B''n + C'',$$

where $A'' = C'$, $B'' = A' + B'$, and $C'' = D'$. The generalization of these expressions to three- and multidimensional networks is straightforward.

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33. The results mentioned in the section "Generalizations and extensions" were suggested by the anonymous referee (August 1995)