Spectral Moments of Polyacenes

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A general expression for the spectral moments of polyacenes is obtained. It is shown that if $h \geq k/2$, then the $(2k)$th spectral moment is an (exact) linear function of h, the number of hexagons.

I. INTRODUCTION

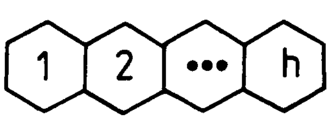
Spectral moments of molecular graphs belong among the traditional tools of the topological theory of conjugated molecules.[1–5] Their best elaborated applications are within the theory of total π-electron energy and of various resonance energies; for some recent work along these lines see refs 6–13. Spectral moments found noteworthy applications also in the physical chemistry of the solid state.[14–17]

The spectral moments of benzenoid molecules have attracted considerable interest by theoretical chemists.[18–21] The dependence of these moments on various structural features of the molecular graph was examined, and appropriate combinatorial formulas were designed for the first 12 moments.[20] In the case of higher moments the same problem seems to be hopelessly complicated, and little progress in this direction could be expected. In view of this, we decided to try to find expressions for the spectral moments of a single homologous series of benzenoid hydrocarbons. A natural choice for this is the polyacenes, because these are the only benzenoids for which the graph eigenvalues are known in explicit analytical form.

Let G be a molecular graph and n the number of its vertices.[2] Then, the eigenvalues of G are just the eigenvalues of the respective adjacency matrix;[2,4] we denote them by $\lambda_1, \lambda_2, ..., \lambda_n$. Then the kth spectral moment of G is defined as

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

Let L_h denote the polyacene with h hexagons. Recall that L_1 = benzene, L_2 = naphthalene, L_3 = anthracene, etc. Note that L_h has $4h + 2$ vertices.



L_h

The eigenvalues of L_h are known[22] since 1948:

$$1, \ -1, \ {}^1/_2 + y_j, \ {}^1/_2 - y_j, \ -{}^1/_2 + y_j, \ -{}^1/_2 - y_j$$

where

$$y_j = {}^1/_2[9 + 8\cos[j\pi/(h+1)]]^{1/2} \tag{1}$$

and $j = 1, 2, ..., h$. Notice that in the above expressions every positive eigenvalue has a negative pair and vice versa. Therefore, for k being an odd-valued integer, $M_k(L_h) = 0$. In view of this, in what follows we shall be concerned only with even values of the parameter k. For k being even, we have

$$M_k(L_h) = 2 + 2\sum_{j=1}^{h} [({}^1/_2 + y_j)^k + ({}^1/_2 - y_j)^k] \tag{2}$$

Equations 1 and 2 fully determine the spectral moments of polyacenes, and no problem seems to exist at all. However, numerical calculations, based on (1) and (2), reveal that, for each fixed value of k, $M_k(L_h)$ is an (exact) linear function of h:

$$M_k(L_h) = \alpha_k h + \beta_k \tag{3}$$

Exceptionally, the simple functional dependence of (3) is violated for the first few values of h. These properties of $M_k(L_h)$ are by no means obvious from (1) and (2). In what follows we demonstrate that eq 3 holds for all even values of k and specify the conditions for its validity. Further, we establish combinatorial expressions for α_k and β_k.

2. STATEMENT OF THE RESULTS

In the subsequent section we show that for all k = 0, 2, 4, 6, ..., and all h = 1, 2, 3, ...

$$M_k(L_h) = \alpha_k h + \beta_k + f_k(h) \tag{4}$$

where α_k and β_k depend only on k and are given by

$$\alpha_k = 2^{2-k}\sum_{r=0}^{k/2}\sum_{s=0}^{\lfloor r/2\rfloor}\binom{k}{2r}\binom{r}{2s}\binom{2s}{s}9^{r-2s}4^{2s} \tag{5}$$

$$\beta_k = 2 - 2^{3-k}\sum_{r=0}^{k/2}\sum_{s=0}^{\lfloor r/2\rfloor}\sum_{u}\binom{k}{2r}\binom{r}{2s}\binom{2s}{u}9^{r-2s}4^{2s} \tag{6}$$

In the above formulas $\lfloor x \rfloor$ denotes the greatest integer that

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is not greater than x (e.g. $\lfloor 3.9\rfloor = 3$, $\lfloor 4.0\rfloor = 4$, $\lfloor 4.1\rfloor = 4$). The third summation in (6) runs over only those values of u, $0 \le u \le s-1, s > 1$, for which $(s-u)/(h+1)$ is not an integer.

The quantity $f_k(h)$, which depends on both k and h, is given by

$$f_k(h) = 2^{3-k}h\sum_{r=0}^{k/2}\sum_{s=0}^{\lfloor r/2\rfloor}\sum_{m=1}^{\lfloor s/(h+1)\rfloor}\binom{k}{2r}\binom{r}{2s}\binom{2s}{s-m(h+1)}9^{r-2s}4^{2s} \qquad (7)$$

and $f_k(h) = 0$ whenever $h \ge \lfloor k/4\rfloor$. Hence, for $h \ge \lfloor k/4\rfloor$ eq 4 reduces to eq 3. For $h < \lfloor k/4\rfloor$, the linear functional dependence between $M_k(L_h)$ and h is violated.

3. PROOF OF FORMULAS 4–7

Expanding the right-hand side of (2) by means of the binomial theorem, we obtain

$$M_k(L_h) = 2 + 2\sum_{j=1}^{h}\left[\sum_{r=0}^{k}\binom{k}{r}\left(\frac{1}{2}\right)^{k-r}[(y_j)^r + (-y_j)^r]\right]$$

which, by taking into account that k is even, is readily transformed into

$$M_k(L_h) = 2 + 2^{2-k}\sum_{j=1}^{h}\sum_{r=0}^{k/2}\binom{k}{2r}(4y_j^2)^r \qquad (8)$$

For the sake of brevity we denote $\pi j/(h+1)$ by θ and $e^{i\theta}$ by ζ. Then $4y_j^2 = 9 + 8\cos\theta$ and

$$(4y_j^2)^r = \sum_{s=0}^{r}\binom{r}{s}9^{r-s}(8\cos\theta)^s = \sum_{s=0}^{r}\binom{r}{s}9^{r-s}4^s(\zeta + 1/\zeta)^s$$

because $\zeta + 1/\zeta = 2\cos\theta$. Expanding $(\zeta + 1/\zeta)^s$, we further obtain

$$(4y_j^2)^r = \sum_{s=0}^{r}\binom{r}{s}9^{r-s}4^s\sum_{u=0}^{s}\binom{s}{u}\zeta^{s-2u} \qquad (9)$$

Now,

$$\binom{s}{u}\zeta^{s-2u} = \binom{s}{s-u}(1/\zeta)^{s-2(s-u)}$$

and therefore

$$\sum_{u=0}^{s}\binom{s}{u}\zeta^{s-2u} = \sum_{u=0}^{\lfloor s/2\rfloor}\left\{\binom{s}{u}[\zeta^{s-2u} + (1/\zeta)^{s-2u}] - \binom{s}{s/2}\delta_u^{s/2}\right\}$$

$$= \sum_{u=0}^{\lfloor s/2\rfloor}\left\{2\binom{s}{u}\cos(s-2u)\theta - \binom{s}{s/2}\delta_u^{s/2}\right\} \qquad (10)$$

where $\delta_u^{s/2} = 1$ if $u = s/2$, and $\delta_u^{s/2} = 0$ otherwise. Combining (8), (9), and (10), we obtain

$$M_k(L_h) = 2 + 2^{2-k}\sum_{r=0}^{k/2}\sum_{s=0}^{r}\sum_{u=0}^{\lfloor s/2\rfloor}\binom{k}{2r}\binom{r}{s}9^{r-s}4^s \times \binom{s}{u}\sum_{j=1}^{h}[2\cos(s-2u)\theta - \delta_u^{s/2}] \qquad (11)$$

Using the trigonometric identity

$$\sum_{j=1}^{h}\cos\phi j = \frac{1}{2}\left[-1 + \sin\left(h + \frac{1}{2}\right)\phi/\sin\frac{1}{2}\phi\right]$$

and recalling that $\theta = \pi j/(h+1)$, we now compute the last summation on the right-hand side of (11), namely,

$$\Omega = \sum_{j=1}^{h}[2\cos(s-2u)\theta - \delta_u^{s/2}]$$

Simple calculation yields the following:

(a) If s is odd, then $\Omega = 0$.

(b) If s is even and $u = s/2$, then $\Omega = h$.

(c) If s is even, $u \ne s/2$, and $(s/2-u)/(h+1)$ is an integer, then $\Omega = 2h$.

(d) If s is even, $u \ne s/2$ and $(s/2-u)/(h+1)$ is not an integer, then $\Omega = -2$.

In view of (a), we see that only even values of s give nonzero contributions to the right-hand side of (11). Then, by neglecting the terms with odd s and by replacing $2s$ by s, we obtain

$$M_k(L_h) = 2 + 2^{2-k}\sum_{r=0}^{k/2}\sum_{s=0}^{\lfloor r/2\rfloor}\binom{k}{2r}\binom{r}{2s}9^{r-2s}4^{2s} \times \sum_{u=0}^{s}\binom{2s}{u}\sum_{j=1}^{h}[2\cos(2s-2u)\theta - \delta_u^s] \qquad (12)$$

By taking into account (b), (c), and (d), the last two summations on the right-hand side of (12) are simplified as

$$\sum_{u=0}^{s}\binom{2s}{u}\sum_{j=1}^{h}[2\cos(2s-2u)\theta - \delta_u^s] = \binom{2s}{s}h + 2h\sum_{m=1}^{\lfloor s/(h+1)\rfloor}\binom{2s}{s-m(h+1)} - 2\sum_u\binom{2s}{u} \qquad (13)$$

In the above formula, Σ_u has the same meaning as in eq 6.

Substituting (13) back into (12) and collecting the terms independent of h ($=\beta_k$), linearly proportional to h ($=\alpha_k h$), and depending on h in a more complicated manner ($=f_k(h)$), we arrive at eqs 4–7.

4. DISCUSSION

The noteworthy property of the function $f_k(h)$, given by eq 7, is that it vanishes for $h \ge \lfloor k/4\rfloor$. To see this, observe that the last summation on the right-hand side of (7) is necessarily zero if $\lfloor s/(h+1)\rfloor < 1$, i.e., if $s < h+1$. Now, because $r_{max} = k/2$ and $s_{max} = \lfloor r_{max}/2\rfloor = \lfloor k/4\rfloor$, the condition $s_{max} < h + 1$ is sufficient enough that the last summation on the right-hand side of (7) is zero for all feasible values of r and s. Consequently, if $s_{max} < h+1$, i.e., if $\lfloor k/4\rfloor < h+1$, i.e. if $h \ge \lfloor k/4\rfloor$, then $f_k(h) = 0$. Consequently, if $h \ge \lfloor k/4\rfloor$, then the kth spectral moment of the polyacene with h hexagons satisfies the simple linear function 3.

The finding that all the spectral moments of L_h increase with h in a linear manner implies that such must be the case also with the total π-electron energy and any of the resonance energies. In fact, the linear h-dependence of these quantities was reported previously, based on computer-generated numerical data.[23,24]

The results obtained in this paper may serve as a guideline in the study of the higher spectral moments of other benzenoid (and, perhaps, also nonbenzenoid) molecules. The rather complicated form of the expressions α_k, β_k, and $f_k(h)$ is a further indication that the resolution of the structure dependency of the higher spectral moments is a difficult task. On the other hand, our results also indicate that a significant simplification of the problem may happen when the consideration is restricted to particular homologous series. As a matter of fact, linear relations between h and the spectral moments were observed in the case of several other series of benzenoid systems. Hence, the relation that we proved in this paper may well be just a special case of a much more general regularity.

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