EIGENVALUES OF LARGE EVEN ANNULENES IN TERMS OF K_3, S_4 AND S_5

Asok K. MUKHERJEE

Chemistry Department, Burdwan Raj College, Burdwan 713104, West Bengal, India

Received 6 November 1987
(in final form 17 March 1988)

Abstract

Squares of the adjacency matrices of bipartite cycles (C_v) can be block-factored into matrices which correspond to vertex-weighted complete graphs for $v = 6$, vertex-weighted strongly regular graphs for $v = 8$ and 10, and vertex-weighted metrically regular graphs for $v > 10$. Using this fact and some properties of strongly and metrically regular graphs, it is shown that eigenvalues of large bipartite C_v graphs (i.e. large even annulenes) can be expressed by the general formula

$$\pm\sqrt{(2 \pm \sqrt{(2 \pm \sqrt{(\ldots \pm \sqrt{(2 + r_p)}) \ldots}),}$$

where $v = 2^n \times p$, n is the number of surd ($\sqrt{}$) signs required and $p = 3, 4$ and 5. Here, r_3, r_4 and r_5 are the eigenvalues of the complete graph K_3 and the strongly regular graphs S_4 and S_5, respectively. The procedure does not require construction of characteristic polynomials for the determination of eigenvalues, and brings out a common topological origin for the two-fold degeneracies observed in the eigenvalue spectra of all even cycles and many odd cycles.

1. Introduction

Graph-theoretical aspects of cyclic conjugated systems have been extensively studied [1–10]. The first requirement in all such studies is the construction of a characteristic polynomial, for which several methods have been devised [11–22]. In the present note, it is shown that eigenvalues of large cycles with an even number of vertices can be expressed in terms of only three cycles: C_3, C_4, and C_5. Of these, C_3 is a complete graph (K_3), C_4 and C_5 are strongly regular [23] graphs (S_4 and S_5), and their eigenvalues are known from their properties. Thus, the construction of a characteristic polynomial is not necessary for obtaining the eigenvalues of large even C_v's. The analysis requires the concept of vertex-weighted graphs, which are used by chemical graph theorists in the treatment of heteroconjugated systems [24–26].

Analytic expressions for eigenvalues and eigenvectors of many symmetric graphs (including annulenes) have been known since the thirties; a very good account of them has been given by Rouvray [27]. Accordingly, the sets of eigenvalues reported here are not new, but the aim is to make use of the spectral properties of complete (K_3) and strongly regular (S_4 and S_5) graphs to obtain eigenvalues and some other graph-spectral features of larger annulenes for the first time.

2. Some regular graphs and their eigenvalues

A *complete* graph is one in which every two vertices are connected by a single edge. For such a graph (K_p) with p vertices, the eigenvalues [28] are $p - 1$ with multiplicity 1, and -1 with multiplicity $p - 1$. Thus, the cyclopropenyl cation has an equilateral triangle (K_3) as its graph and its eigenvalues are $2, -1, -1$. The white phosphorus molecule P_4, with a tetrahedral structure, has K_4 as its molecular graph and eigenvalues $3, -1, -1, -1$.

The concept of a *strongly regular* graph was introduced by Bose [23], and Cameron has given a good account of such graphs in [29]. A graph (S_p) of p vertices is said to be strongly regular if there exist k, β and μ such that:

(i) each vertex has valency k,

(ii) given any two distinct vertices v and w, the number of vertices adjacent to both v and w is β if v and w are adjacent and μ otherwise.

Among the Hückel annulenes, only cyclobutadiene, having a sqaure as the molecular graph ($k = 2, \beta = 0, \mu = 2$) and the cyclopentadienyl anion, having a regular pentagon as the molecular graph ($k = 2, \beta = 0, \mu = 1$), are strongly regular. According to the "integrality condition" [18], the eigenvalues of such graphs are k and $\frac{1}{2}[\beta - \mu \pm \sqrt{[(\beta - \mu)^2 + 4(k - \mu)]}]$; the latter two roots r and s, corresponding to the "+" and "−" signs, respectively, have multiplicities f and g, respectively, such that

$$f + g = p - 1 \quad \text{and} \quad k + fr + gs = 0, \tag{1}$$

where p is the number of vertices. Thus, the eigenvalues of cyclobutadiene (S_4) are $2, 0, 0, -2$ and those of the cyclopentadienyl anion (S_5) are $2, -\frac{1}{2}(1 + \sqrt{5}), -\frac{1}{2}(1 + \sqrt{5}), \frac{1}{2}(\sqrt{5} - 1), \frac{1}{2}(\sqrt{5} - 1)$.

A connected graph is said to be *metrically regular* [29] if there are integers p_{ij}^k such that whenever v and w are vertices at distance k, the number of vertices at distance i from v and j from w is equal to p_{ij}^k. Thus, all Hückel annulenes (having C_n graphs) with at least six conjugated carbon atoms have metrically regular graphs. For example, in benzene, $p_{11}^1 = 2, p_{23}^1 = 1$, etc.

3. Block-factorisation of bipartite graphs and regularity of the factors for cycles

The formal study of bipartite graphs originated in a chemical context when Coulson and Rushbrooke proved their famous pairing theorem [30]. The vertices of such graphs can be marked with asterisks alternatively. If the unstarred vertices are labelled $1, 2, \ldots$ and the starred ones $1^*, 2^*, \ldots$ etc., the adjacency matrix (A) of the graph has the form:

$$A = \begin{bmatrix} \hat{0} & B \\ B^t & \hat{0} \end{bmatrix},$$

where $\hat{0}$ is the null matrix of adequate size and B^t is the transpose of B. The occurrence of null matrices is a result of the fact that no two vertices of the same set (starred or unstarred) are connected. Now, the square of the matrix A will be block-factored as

$$A^2 = \begin{bmatrix} R_1 & \hat{0} \\ \hat{0} & R_2 \end{bmatrix}.$$

The (ij) element of A^2 is the number of walks of length 2 from the ith vertex to the jth vertex. However, the distance from any starred vertex to any unstarred vertex is either 1 or greater than 2. This explains the appearance of the blocks of null matrices in A^2. The eigenvalues of A can be obtained from those of A^2 by utilizing the following well-known result of matrix algebra [31]:

If Ψ is any polynomial and if β is any eigenvalue of the matrix A, then $\Psi(\beta)$ is an eigenvalue of the matrix $\Psi(A)$.

Thus, if $\pm\sqrt{\beta}$ be any two eigenvalues of A, then A^2 must have eigenvalue β. It is convenient to follow the reverse way, since A^2 is block-factored and its eigenvalues are those of the smaller matrices R_1 and R_2.

In the case of bipartite cycles, the factor matrices R_1 and R_2 provide us with additional advantages:

(1) Bipartite cycles must have an even number of vertices so that there are equal numbers of starred and unstarred vertices. Hence, R_1 and R_2 have equal numbers of eigenvalues. Again, A^2 and A have equal numbers of eigenvalues since they are of the same size, but each eigenvalue of A^2 corresponds to two eigenvales of A. Also, the set of eigenvalues of A^2 is the combined set of eigenvalues of R_1 and R_2 (because of block-factorisation). In fact, $R_1 = R_2$, and to obtain the eigenvalues of A, one needs to find only those of R_1.

(2) Each vertex of a cycle is of degree 2. Hence, each diagonal element in R_1 and R_2 is 2. The alternate starring scheme also suggests that the number of walks of length 2 between any two distinct vertices of the same set (starred or unstarred) must be either 1 or 0. Thus, R_1 and R_2 are square matrices with 1 and 0 as off-diagonal elements. From each of these, we can therefore construct a vertex-weighted graph, giving each vertex a weight 2. These derived graphs will, however, be unique only up to isomorphism but this will not affect the final evaluation of the eigenvalues. Table 1 shows the factor matrix R_1 obtained from A^2 for some bipartite Hückel annulenes.

Table 1

R_1 derived from the squares of adjacency matrices of some bipartite molecular graphs

Molecule	R_1
Benzene	$\begin{bmatrix} 2 & 1 & 1 \\ 1 & 2 & 1 \\ 1 & 1 & 2 \end{bmatrix} = A(K_3) + 2I_3$
8-annulene	$\begin{bmatrix} 2 & 1 & 0 & 1 \\ 1 & 2 & 1 & 0 \\ 0 & 1 & 2 & 1 \\ 1 & 0 & 1 & 2 \end{bmatrix} = A(S_4) + 2I_4$
10-annulene	$\begin{bmatrix} 2 & 1 & 0 & 0 & 1 \\ 1 & 2 & 1 & 0 & 0 \\ 0 & 1 & 2 & 1 & 0 \\ 0 & 0 & 1 & 2 & 1 \\ 1 & 0 & 0 & 1 & 2 \end{bmatrix} = A(S_5) + 2I_5$

In the matrices $A(S_4)$ and $A(S_5)$, the vertices of S_4 and S_5 have been enumerated consecutively and not alternately.

4. Determination of eigenvalues

Benzene (C_6): The matrix R_1 for benzene is simply the adjacency matrix $A(K_3)$ of the complete graph K_3 corresponding to the cyclopropenyl cation, with each diagonal 0 being replaced by 2. Hence, R_1 in this case corresponds to a vertex-weighted complete graph and we find $R_1 = A(K_3) + 2I_3$, where I_3 is the 3×3 unit matrix. For a symmetric matrix $B' = B + hI$, the eigenvalues (β') are those (β) of B, each raised by h units since the characteristic equation $\det(\beta' I - B') = 0$ implies

$$\det[(\beta' - h)I - B] = 0,$$

giving $\beta' - h = \beta$. In the context of Hückel theory, this corresponds to a shifting of the zero of energy from α (the Coulomb integral of benzene carbon) to $\alpha + h$. Thus, the eigenvalues of R_1 are those of K_3, each raised by 2 units, i.e. 4, 1, 1. Consequently, benzene has eigenvalues $\pm 2, \pm 1, \pm 1$.

8- and 10-annulenes (C_8 and C_{10}): For 8-annulene, R_1 is the adjacency matrix of cyclobutadiene, each diagonal 0 being raised by 2, i.e. $R_1 = A(S_4) + 2I_4$. By the same argument as before, the eigenvalues of R_1 are those of S_4, each raised by 2. Thus, 8-annulene has eigenvalues $\pm 2, \pm\sqrt{2}, \pm\sqrt{2}, 0, 0$.

For 10-annulene, $R_1 = A(S_5) + 2I_5$ and the eigenvalues are $\pm 2, \pm\sqrt{[(3 - \sqrt{5})/2]}$, $\pm\sqrt{[(3 - \sqrt{5})/2]}$, $\pm\sqrt{[(3 + \sqrt{5})/2]}$, $\pm\sqrt{[(3 + \sqrt{5})/2]}$.

12-annulene (C_{12}): Here, $R_1 = A(C_6) + 2I_6$, where $A(C_6)$ is the adjacency matrix of the metrically regular graph of benzene. The eigenvalues of R_1 will, therefore, be those of benzene (obtained earlier) raised by 2, and so 12-annulene has eigenvalues $\pm 2, 0, 0, \pm\sqrt{3}, \pm\sqrt{3}, \pm 1, \pm 1$.

It is now clear that the process may be used recursively to obtain eigenvalues of all the even annulenes. It does not require construction of characteristic polynomials. In constructing the adjacency matrices $A(S_4)$, $A(S_5)$, $A(S_6)$ – from the graphs of cyclobutadiene, the cyclopentadienyl anion and benzene, respectively, – the vertices have been enumerated consecutively and not alternately. In fact, it is easy to show that for any C_n with an eigenvalue r_n,

$$A^2(C_{2n}) = \begin{bmatrix} A(C_n) + 2I_n & \hat{0} \\ \hat{0} & A(C_n) + 2I_n \end{bmatrix},$$

from which it immediately follows that

$$r_{2n} = \pm\sqrt{(2 + r_n)}. \tag{2}$$

For $n = 3, 4$ and 5, the eigenvalues r_n and their multiplicities are known from eq. (1). For larger even cycles, one can iterate eq. (2) until one ends with $n = 3, 4$ or 5. Thus,

$$r_{12n} = \pm\sqrt{(2 + r_6)} = \pm\sqrt{(2 \pm \sqrt{(2 + r_3)})}.$$

The eigenvalues obtained by the present procedure are in full agreement with those obtained from the general formula $2\cos(2\pi j/n)$, $j = 1, 2, \ldots, n$ for Hückel n-annulenes.

The obtained results are summarized in table 2. It is clear from this table that the eigenvalues of a cycle C_υ, with $\upsilon = 2^n \times p$ ($p = 3, 4, 5$) are obtainable from the general formula

Table 2

Eigenvalues of some even annulenes in terms of those of K_3, S_4 and S_5

Annulene	Number of vertices	Eigenvalues*
Benzene	3×2^1	$\pm\sqrt{[2+r_3]}$
12-annulene	3×2^2	$\pm\sqrt{[2\pm\sqrt{[2\pm r_3]}]}$
24-annulene	3×2^3	$\pm\sqrt{[2\pm\sqrt{[2\pm r_3]}]}$
8-annulene	4×2^1	$\pm\sqrt{[2\pm r_4]}$
16-annulene	4×2^2	$\pm\sqrt{[2\pm\sqrt{[2\pm r_4]}]}$
32-annulene	4×2^3	$\pm\sqrt{[2\pm\sqrt{[2\pm\sqrt{[2+r_4]}]}]}$
10-annulene	5×2^1	$\pm\sqrt{[2\pm r_5]}$
20-annulene	5×2^2	$\pm\sqrt{[2\pm\sqrt{[2+r_5]}]}$

*r_3, r_4 and r_5 are eigenvalues of K_3, S_4 and S_5, respectively.

$$\pm\sqrt{[2\pm\sqrt{[2\pm\sqrt{[2\pm\ldots\pm\sqrt{[2+r_p]}]}\ldots]}}, \tag{3}$$

where the number of surd signs ($\sqrt{}$) required is n, and r_p is an eigenvalue of K_3, S_4 or S_5 according to whether $p = 3, 4$ or 5.

The following important inferences can be drawn from the present correlation of large even annulenes to K_3, S_4 and S_5:

(a) These three special cycles show only twofold degeneracy in their spectra. Hence, larger annulenes which can be correlated with them must also show only twofold degeneracy in their eigenvalue spectra – a well-known feature of monocyclic conjugated hydrocarbons on which Hückel's $(4n + 2)$ rule of aromaticity is based [32,33].

(b) As the topological matrix is Hermitian, r_{2n} must be real and from eq. (2) it immediately follows that $|r_n| < 2$ for any n. Thus, for any cycle the largest eigenvalue should not exceed 2. This is also consistent with the "chromatic number rule" for largest eigenvalues [34], since annulenes are at most tripartite.

(c) The largest eigenvalue of K_3, S_4 or S_5 is 2, and the recursive expression (3) shows that for any even annulene the largest eigenvalue should be 2.

In conclusion, we mention that the eigenvalues of large cycles can be correlated with smaller ones in a variety of ways. Thus, it is easy to show that for any C_{3n} (with arbitrary integer $n > 1$)

$$r_{3n} = f(r_n), \tag{4}$$

where $f(a)$ is any one of the roots x of the equation

$$x^3 - 3x - a = 0. \tag{5}$$

In this language, eq. (2) can be stated as

$$r_{2n} = g(r_n),$$

where $g(a)$ satisfies $x^2 - 2 - a = 0$. In general, for a cycle C_{mn}, the analogous equation is

$$r_{mn} = F_m(r_n),$$

where $F_m(a)$ is any one of the roots of a suitable m-degree polynomial. However, the advantage with $m = 2$, which has been used here, is that the quadratic equations can be solved by "radicals" and that r_n, which is to be substituted for a, is known from the special properties, e.g. completeness of C_3 and strong regularity of C_4 and C_5.

Equations (4) and (5) are also very interesting. The roots of (5) are of the form:

$$x = f(a) = [\tfrac{1}{2}(a + \sqrt{(a^2 - 4)})]^{1/3} + [\tfrac{1}{2}(a + \sqrt{(a^2 - 4)})]^{1/3}.$$

Hence, any odd annulene of size 3^n or $3^n \cdot 5$ will inherit some characteristics of C_3 and C_5, respectively. For example, $a = 2$ gives $r_9 = f(r_3) = 2$ as the largest eigenvalue of C_9. Thus, recursively, all odd annulenes of the above two types will have 2 as the largest eigenvalue and the other eigenvalues will show only twofold degeneracy.

Acknowledgement

The author expresses his thanks to the referees for their valuable comments, particularly for the concluding section of this paper.

References

[1] A. Graovac, I. Gutman, N. Trinajstić and T. Živković, Theor. Chim. Acta 26(1972)67.
[2] I. Gutman, M. Milun and N. Trinajstić, J. Amer. Chem. Soc. 99(1975)1692.
[3] P. Ilić, B. Sinković and N. Trinajstić, Israel J. Chem. 20(1980)258.
[4] I. Gutman, Theor. Chim. Acta 56(1980)89.
[5] I. Gutman and O.E. Polansky, Theor. Chim. Acta 60(1981)203.
[6] N. Ohkami and H. Hosoya, Theor. Chim. Acta 64(1983)153.
[7] I. Gutman, Theor. Chim. Acta 66(1984)43.
[8] I. Gutman, A.V. Teodorović and L. Nedeljković, Theor. Chim. Acta 65(1984)23.
[9] K. Sakuri, K. Kitaura and K. Nishimoto, Theor. Chim. Acta 69(1986)23.
[10] A.K. Mukherjee, Indian J. Chem. 25A(1986)574.

[11] H. Sachs, Publ. Math. (Debrecen) 9(1962)270.
[12] J. Aihara, J. Amer. Chem. Soc. 98(1976)6840.
[13] H. Hosoya, Theor. Chim. Acta 25(1972)215.
[14] M. Randić, SIAM J. Alg. Disc. Math. 6(1985)145.
[15] K. Balasubramanian, Theor. Chim. Acta 65(1984)49.
[16] K. Balasubramanian, J. Comput. Chem. 3(1984)587.
[17] R. Ramaraj and K. Balasubramanian, J. Comput. Chem. 6(1985)122.
[18] M. Randić, J. Comput. Chem. 3(1982)421.
[19] M. Randić, Theor. Chim. Acta 62(1983)485.
[20] M. Randić, J. Math. Chem. 1(1987)145.
[21] R. Barakat, Theor. Chim. Acta 69(1986)35.
[22] F. Kŕivka, Ž. Jeričević and N. Trinajstić, Int. J. Quant. Chem. S19(1985)129.
[23] R.C. Bose, Pacifico J. Math. 13(1963)389.
[24] R.B. Mallion, A.J. Schwenk and N. Trinajstić, Croat. Chem. Acta 46(1974)171.
[25] A. Graovac, O.E. Polansky, N. Trinajstić and N. Tyutylkov, Z. Naturforsch. 30a(1975)1696.
[26] M.J. Rigby, R.B. Mallion and A.C. Day, Chem. Phys. Lett. 51(1977)178.
[27] D.H. Rouvray, in: *Chemical Applications of Graph Theory*, ed. A.T. Balaban (Academic Press, London, 1976) p. 175.
[28] W.L. Beineke and R.J. Wilson, eds., *Selected Topics in Graph Theory* (Academic Press, London, 1978) p. 317.
[29] See pp. 337 – 360 of ref. [28].
[30] C.A. Coulson and G.S. Rushbrooke, Proc. Cambridge Phil. Soc. 36(1940)193.
[31] See p. 309 of ref. [28].
[32] E. Hückel, Z. Phys. 70(1931)204; 76(1932)628.
[33] E. Hückel, Z. Elektrochem. 43(1937)752.
[34] See pp. 300 – 331 of ref. [28].