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SPECTRAL PROPERTIES OF SOME GRAPHS DERIVED FROM BIPARTITE GRAPHS

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Abstract: Let G be a bipartite graph with a vertices: v_1, v_2 ..., v_a of the first colour and b vertices: v_{a+1}, v_{a+2}, ..., v_{a+b} of the second colour. Let K and H be two rooted graphs. Then the graph G{K,H} is obtained by identifying each of the vertices v_i; i = 1, ..., a with the root of a copy of K, and by identifying each of the vertices v_i, i = a+1, ..., a+b with the root of a copy of H.

The main result of the paper (Theorem 1) relates the characteristic polynomials of G, K and H with the characteristic polynomial of G{K,H}. Analogous relations are shown to hold also for the matching polynomials of these graphs (Theorem 2).

The spectra of various classes of graphs are determined.

1. Introduction

Explicite analytical expressions are known for the eigenvalues of numerous classes of molecular graphs or, what is equivalent, for the Hückel molecular orbital (HMO) energies of the corresponding classes of conjugated molecules [1,2]. In certain cases when the molecular graph possesses symmetry, the eigenvalue problem can be solved by means of group theoretical arguments [3-6]. Besides, several graph theoretical techniques have been recently elaborated which enable the factorization of the characteristic polynomial of some compound graphs without the (explicite) use of group theory [7-10]. In the present paper we offer a further result of this type.

We shall use the following notation and terminology. G will always denote a bipartite (but otherwise arbitrary) graph with a vertices of the first colour (which will be labelled by v_1, v_2, ..., v_a) and b vertices of the second colour (which will be labelled by v_{a+1}, v_{a+2}, ..., v_{a+b}). Hence the vertices v_1, v_2, ..., v_a (and also v_{a+1}, v_{a+2}, ..., v_{a+b}) are not mutually connected.

It will be assumed that $a \leq b$ and $a + b = n$.

The characteristic polynomial of G is denoted by $\phi(G) = \phi(G,x)$. Its zeros form the spectrum of the graph G, which will be denoted as

$$Sp(G) = \{x_1, x_2, \ldots, x_n\},$$

where the x_j's, $j = 1,2,\ldots,n$ are the eigenvalues of G and by convention

$$x_1 \geq x_2 \cdots \geq x_n.$$

It is well known that the eigenvalues of a bipartite graph are paired, i.e.

$$x_j = x_{n+1-j} \quad \text{for } j = 1,2,\ldots,n$$

and that at least b-a among them are equal to zero [2]. Therefore,

$$\phi(G) = \prod_{j=1}^{n} (x-x_j) = x^{b-a} \prod_{j=1}^{a} (x^2-x_j{}^2). \tag{1}$$

Let e be an edge of G, connecting the vertices v and w. Then the following recurrence relation holds for the characteristic polynomial of G.

$$\phi(G) = \phi(G-e) - \phi(G-v-w) - 2 \sum_{C} \phi(G-C) \tag{2}$$

The summation in the above formula goes over all cycles C which are contained in G. For the following discussion it will be important that if G is bipartite, then also all the subgraphs appearing on the right side of (2) are bipartite.

Further spectral properties of graphs the reader may find in the book [2].

The matching polynomial of G will be denoted by $\alpha(G) = \alpha(G,x)$ Its definition and basic properties can be found elsewhere [11]. The zeros of $\alpha(G)$ form the A-spectrum of the graph G,

$$Sp_A(G) = \{y_1, y_2, \ldots, y_n\}.$$

It is known that the A-spectrum of every graph is real [11,12] and we may adopt the convention

$$y_1 \geq y_2 \geq \cdots \geq y_n.$$

From the definition [11] of $\alpha(G)$ it follows that

$$y_j = y_{n+1-j} \quad \text{for} \quad j = 1,2, \ldots, n$$

and at least b-a elements of $Sp_A(G)$ are equal to zero. Therefore,

$$\alpha(G) = \prod_{j=1}^{n} (x-y_j) = x^{b-a} \prod_{j=1}^{a} (x^2-y_j{}^2). \tag{3}$$

The matching polynomial conforms to the recurrence relation

$$\alpha(G) = \alpha(G-e) - \alpha(G-v-w), \tag{4}$$

which is analogous to eq. (2)

Let R_1, R_2, ..., R_n be a collection of $n = a+b$ distinct rooted graphs.* Let R_i^* denotes the subgraph obtained by deleting the root from R_i.

<u>Definition 1</u>: The graph $G\{R_1,R_2,...,R_n\}$ is obtained by simultaneous identification of the root of R_i with v_i, $i = 1,2,...,n$.

Godsil and McKay [10] have examined the spectrum of $G\{R_1,R_2...,R_n\}$ in the general case when all the graphs R_i may be mutually non-isomorphic. They proved that if $\underset{\sim}{A} = ||A_{ij}||$ is the adjacency matrix of the graph G, then

$$\phi(G\{R_1,R_2,...,R_n\}) = \det \underset{\sim}{B}, \tag{5}$$

where $\underset{\sim}{B} = ||B_{ij}||$ is a square matrix of order n whose matrix elements are defined as

$$B_{ij} = \begin{cases} -A_{ij}\ \phi(R_j^*) & \text{if} \quad i \neq j \\ \phi(R_j) & \text{if} \quad i=j. \end{cases}$$

Note that for Definition 1 and formula (5) it is immaterial whether the graph G is bipartite or not.

If G is bipartite, we can introduce the following specialization.

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* A graph is said to be rooted if one of its vertices is distinguished by a particular label. Otherwise a rooted graph and its (unrooted) parent graph have exactly the same properties.

In particular, a rooted graph has the same characteristic and matching polynomial as its parent graph.

The distinguished vertex of a rooted graph is called the root.

<u>Definition 2</u>: The graph G{K,H} is the special case of $G\{R_1,R_2,...,R_n\}$ when $R_1 = R_2 = ... = R_a = K$ and $R_{a+1} = R_{a+2} = ... = R_{a+b} = H$.

Note that for a=b, Definition 2 determines a unique graph G{K,H} only if the vertices of G are labelled. If a < b, G{K,H} is unique also when G is an unlabelled graph. Note also that K and H need not be bipartite graphs.

<u>Definition 3</u>: The graph G{H} is the special case of G{K,H} when K = H.

In the following we shall focus our attention to the graphs of the form G{K,H}. If K and H possess n_1 and n_2 vertices, respectively, then G{K,H} possesses $an_1 + bn_2$ vertices. Two examples of graphs G{K,H} are given in Fig. 1; we immediately see that G{K,H}≠G{H,K}.

2. The Main Theorem

Let K* and H* denote the subgraphs obtained from K and H, respectively, by deleting their roots. Then our main result is the following

<u>Theorem 1</u>:

$$\phi(G[K,H]) = [\phi(H)/\phi(K)]^{(b-a)/2}[\phi(K^*)\phi(H^*)]^{(a+b)/2} \cdot$$
$$\cdot \phi(G,[\phi(K)\phi(H)/\phi(K^*)\phi(H^*)]^{1/2}) \quad (6)$$

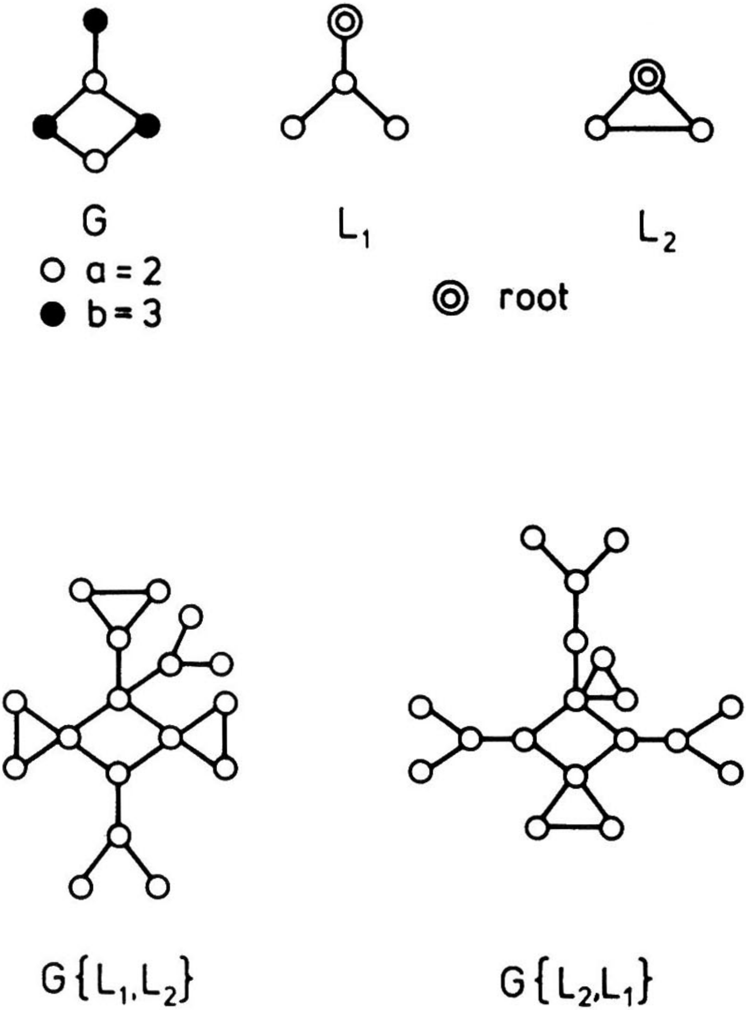


Fig. 1

and

$$\phi(G[K,H]) = \phi(H)^{b-a} \prod_{j=1}^{a} [\phi(K)\phi(H) - x_j^2 \phi(K^*)\phi(H^*)]. \tag{7}$$

Example: For the graphs $G\{L_1,L_2\}$ and $G\{L_2,L_1\}$ from Fig. 1 the application of eq. (7) gives

$$\phi(G\{L_1,L_2\}) = (x^3-3x-2)\ [(x^4-3x^2)(x^3-3x-2) -$$
$$- \frac{5+\sqrt{17}}{2}(x^3-2x)(x^2-1)][(x^4-3x^2)(x^3-3x-2) - \frac{5-\sqrt{17}}{2}(x^3-2x)(x^2-1)]$$

and

$$\phi(G\{L_2,L_1\}) = (x^4-3x^2)[(x^4-3x^2)(x^3-3x-2) - \frac{5+\sqrt{17}}{2}(x^3-2x)(x^2-1)]$$
$$[(x^4-3x^2)(x^3-3x-2) - \frac{5-\sqrt{17}}{2}(x^3-2x)(x^2-1)]$$

since $\phi(L_1) = x^4-3x^2$, $\phi(L_2) = x^3-3x-2$, $\phi(L_1^*) = x^3-2x$,

$\phi(L_2^*) = x^2-1$ and

$$Sp(G) = \{\sqrt{\frac{5+\sqrt{17}}{2}}, \sqrt{\frac{5-\sqrt{17}}{2}}, 0, -\sqrt{\frac{5-\sqrt{17}}{2}}, -\sqrt{\frac{5+\sqrt{17}}{2}}\}.$$

Before we proceed to prove this Theorem we point at a number of its interesting consequences and special cases.

Corollary 1: If K = H (and therefore also $K^* = H^*$), eqs, (6) and (7) are significantly simplified:

$$\phi(G\{H\}) = \phi(H^*)^n \phi(G, \phi(H)/\phi(H^*)),$$

$$\phi(G\{H\}) = \prod_{j=1}^{n} [\phi(H)-x_j\phi(H^*)].$$

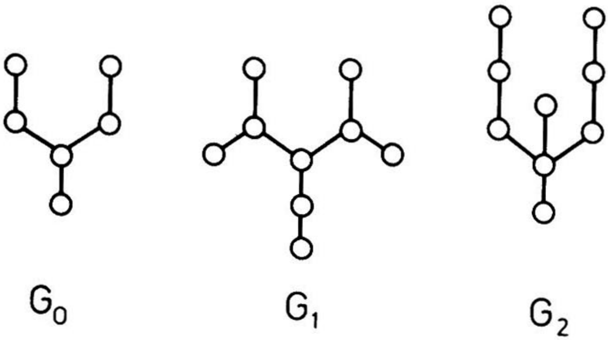
These results have been previously derived by Schwenk [13]. They hold for both bipartite and non-bipartite graphs.

Corollary 2: Sp(G{K,H}) contains at least b-a times the entire spectrum of H.

Corollary 3: $\phi(G\{K,H\})\phi(K)^{b-a} = \phi(G\{H,K\})\phi(H)^{b-a}$.

In particular, if a=b, then the graphs G{K,H} and G{H,K} are isospectral for arbitarary K and H.

The two simplest nonisomorphic isospectral graphs which can be constructed in this manner are $G_1 = G_o\{P_2,P_1\}$ and $G_2 = G_o\{P_1,P_2\}$.



In the above example and in the following, P_n denotes the path with n vertices.

<u>Corollary 4</u>: The graph $G\{K,P_1\}$ is obtained by joining the graphs K to the vertices of the first colour, but joining nothing to the vertices of the second colour. Then eq. (7) becomes

$$\phi(G\{K,P_1\}) = x^{b-a} \prod_{j=1}^{a} [x\phi(K)-x_j{}^2\phi(K^*)]$$

Similarly

$$\phi(G\{P_1,H\}) = \phi(H)^{b-a} \prod_{j=1}^{a} [x\phi(H)-x_j{}^2\phi(H^*)].$$

In particular

$$\phi(G\{P_2,P_1\}) = x^b \prod_{j=1}^{a} (x^2-x_j^2-1),$$

$$Sp(G\{P_2,P_1\}) = \{\pm\sqrt{x_j^2+1} \mid j=1,\ldots,a\} \cup \{0,\ b \text{ times}\},$$

$$\phi(G\{P_1,P_2\}) = x^a(x^2-1)^{b-a} \prod_{j=1}^{a} (x^2-x_j^2-1).$$

$$Sp(G\{P_1,P_2\}) = \{\pm\sqrt{x_j^2+1} \mid j=1,\ldots,a\} \cup \{0,\ a \text{ times}\} \cup$$

$$\cup \{\pm 1,\ b-a \text{ times}\}.$$

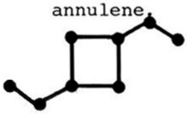
<u>Examples</u>: Let S_{d+1} denotes the star with d+1 vertices ($d > 1$), rooted at one of its vertices of degree one. Then from Corollary 4,

$$Sp(G\{S_{d+1},P_1\}) = \{\pm\sqrt{\tfrac{1}{2}(d+x_j^2 \pm \sqrt{(d-x_j^2)^2 + 4x_j^2})} \mid j =$$

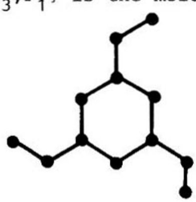
$$= 1,\ldots,a\} \cup \{0,\ (d-2)a+b-a \text{ times}\}.$$

For G being the cycle C_{2a} with 2a vertices and d=2, we obtain the molecular graph of [2a]annulene which is substituted with vinyl groups at the positions 1,3,...,2a-1. In the following we shall refer to such derivatives of annulenes as s-substituted annulenes.

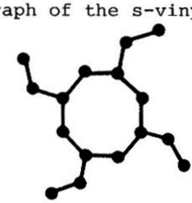
Hence, $C_{2a}\{S_3,P_1\}$ is the molecular graph of the s-vinyl[2a]-annulene.



$C_4\{S_3,P_1\}$



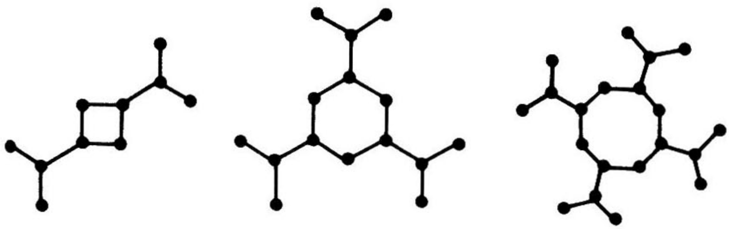
$C_6\{S_3,P_1\}$



$C_8\{S_3,P_1\}$

$$Sp(C_{2a}\{S_3,P_1\}) = \{\pm[2\cos^2 \frac{j\pi}{a} + 1 \pm \sqrt{4\cos^4 \frac{j\pi}{a} + 1}]^{1/2} \mid j=1,..,a\}. \quad (8)$$

The molecular graph of s-allyl[2a]annulene is $C_{2a}\{S_4,P_1\}$.



$C_4\{S_4,P_1\}$ $C_6\{S_4,P_1\}$ $C_8\{S_4,P_1\}$

$$Sp(C_{2a}\{S_4,P_1\}) = \{\pm\frac{\sqrt{2}}{2}[3+4\cos^2 \frac{j\pi}{a} \pm\sqrt{(3-4\cos^2 \frac{j\pi}{a})^2 + 16\cos^2 \frac{j\pi}{a}}]^{1/2}$$
$$\mid j=1,...,a\} \bigcup \{0, \text{ a times}\}. \quad (9)$$

In order to prove Theorem 1 we need the following auxiliary result.

Let G be a bipartite graph with a+b vertices as defined before. Then G{k,h} is obtained from G by attaching a self-loop of the weight k to all the vertices $v_1,v_2,...,v_a$ and a self-loop of the weight h to all the verices v_{a+1}, v_{a+2}, ..., v_{a+b}. The weights k and h may have arbitrary numerical values.

Lemma 1:

$$\phi(G\{k,h\}) = \left(\frac{x-k}{x-h}\right)^{(b-a)/2} \phi(G,\sqrt{(x-k)(x-h)}).$$

Proof will be performed by induction on the number of edges of the graph G.

In order to simplify our notation we introduce the variables T and t as follows:

$$T = \left(\frac{x-h}{x-k}\right)^{(b-a)/2} \; ; \quad t = \sqrt{(x-k)(x-h)}.$$

For the graph O_n without edges and with a+b=n vertices the Lemma holds because of

$$\phi(O_n) = x^n$$

$$\phi(O_n\{k,h\}) = (x-k)^a \; (x-h)^b.$$

Assume that Lemma holds for all bipartite graphs with less than m edges. Let G possesses m edges. Then the application of eq (2) gives

$$\phi(G\{k,h\}) = \phi(G\{k,h\}-e) - \phi(G\{k,h\}-v-w) - 2\sum_C \phi(G\{k,h\}-C) =$$

$$= \phi((G-e)\{k,h\}) - \phi((G-v-w)\{k,h\}) - 2\sum_C \phi((G-C)\{k,h\}).$$

The graphs G-e, G-v-w and G-C are bipartite, possess less than m edges and have the same difference b-a as G. Therefore,

$$\phi(G\{k,h\}) = T[\phi(G-e,t)-\phi(G-v-w,t)-2\sum_C \phi(G-C,t)] = T\phi(G,t). \quad \text{Q.E.D.}$$

It should be mentioned that a formula equivalent to our Lemma (in fact its special case when k=0 and a=b) was known to Bochvar et al. [14]. However, these authors have never published a proof of their result.

Proof of Theorem 1: Let us write the characteristic polynomial of K and H in the form

$$\phi(K) = (x-k)\ \phi(K^*), \qquad (10)$$

$$\phi(H) = (x-h)\ \phi(H^*), \qquad (11)$$

where k and h are adjusted parameters (which depend on the variable x).

The characteristic polynomial of G{K,H} can be calculated from eq. (5) by setting $R_1=R_2=\ldots=R_a=K$, $R_{a+1}=R_{a+2}=\ldots=R_{a+b}=H$. Taking into account the relations (10) and (11) one gets

$$\phi(G\{K,H\}) = \phi(K^*)^a\ \phi(H^*)^b \cdot \det\left[\begin{pmatrix}(x-k)\,\underset{\sim}{I}_a & \underset{\sim}{0} \\ \underset{\sim}{0} & (x-h)\,\underset{\sim}{I}_b\end{pmatrix} - \underset{\sim}{A}\right]$$

where $\underset{\sim}{I}_a$ and $\underset{\sim}{I}_b$ are unit matrices of order a and b, respectively and $\underset{\sim}{0}$ is a zero matrix. On the other hand,

$$\det\left[\begin{pmatrix}(x-k)\,\underset{\sim}{I}_a & \underset{\sim}{0} \\ \underset{\sim}{0} & (x-h)\,\underset{\sim}{I}_b\end{pmatrix} - \underset{\sim}{A}\right]$$

is just the characteristic polynomial of G{k,h}, i.e.

$$\phi(G\{K,H\}) = \phi(K^*)^a\ \phi(H^*)^b\ \phi(G\{k,h\}).$$

Eq. (6) follows now immediately from Lemma 1. Eq. (7) is then obtained by applying (1). Q.E.D.

3. An Application of Lemma 1

Lemma 1 can be presented also in the form

$$\phi(G\{k,h\}) = (x-h)^{b-a} \prod_{j=1}^{a} [(x-k)(x-h)-x_j^2]$$

from which the spectrum of G{k,h} can be easily determined. In particular,

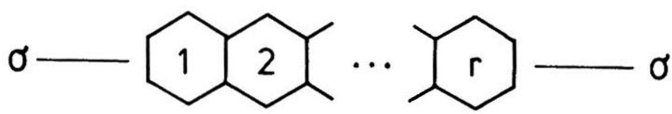
$$Sp(G\{0,\pm 1\}) = \{\tfrac{1}{2}(\pm 1+\sqrt{1+4x_j^2}),\ \tfrac{1}{2}(\pm 1-\sqrt{1+4x_j^2})\ |$$

$$|\ j=1,\dots,a\} \bigcup \{\pm 1,\ b-a \text{ times}\}, \qquad (12a)$$

$$Sp(G\{\pm 1,0\}) = \{\tfrac{1}{2}(\pm 1+\sqrt{1+4x_j^2}),\ \tfrac{1}{2}(\pm 1-\sqrt{1+4x_j^2})\ |$$

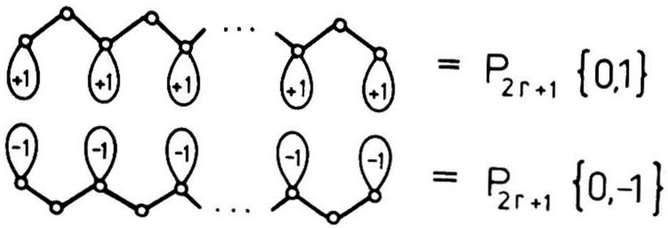
$$|\ j=1,\dots,a\} \bigcup \{0,\ b-a \text{ times}\}. \qquad (12b)$$

Let us consider the linear polyacene L_r with r rings.



L_r

It possesses a plane of symmetry σ. According to the well known rules [3], $\phi(L_r)$ is factorized into $\phi(P_{2r+1}\{0,1\})$ and $\phi(P_{2r+1}\{0,-1\})$.



Since $Sp(P_{2r+1}) = \{2\cos\frac{j\pi}{2r+2} \mid j=1,\ldots,2r+1\}$,

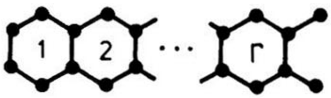
we can determine the graph spectrum of the linear polyacene using eqs. (12a).

$\phi(L_r)=\phi(P_{2r+1}\{0,1\})\phi(P_{2r+1}\{0,-1\})$,

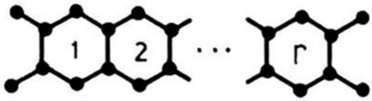
$Sp(L_r) = \{\pm\frac{1}{2}(\sqrt{9+8\cos\frac{\pi j}{r+1}} \pm 1) \mid j=1,\ldots,r\}\cup\{1,-1\}$.

This result is, of course, well known [1,5].

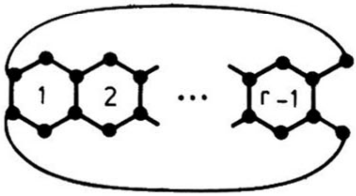
In an analogous manner we can deduce also the spectra of the following molecular graphs.



LA_r



LB_r



LC_r

$\phi(LA_r)=\phi(P_{2r+2}\{0,1\})\phi(P_{2r+2}\{0,-1\})$,

$\phi(LB_r)=\phi(P_{2r+3}\{1,0\})\phi(P_{2r+3}\{-1,0\})$,

$\phi(LC_r)=\phi(C_{2r}\{1,0\})\phi(C_{2r}\{-1,0\})$,

$$Sp(LA_r)=\{\pm\frac{1}{2}(\sqrt{9+8\cos\frac{\pi j}{r+3/2}}\pm 1)\ |j=1,\ldots,r+1\},$$

$$Sp(LB_r)=\{\pm\frac{1}{2}(\sqrt{9+8\cos\frac{\pi j}{r+2}}\pm 1)\ |j=1,\ldots,r+1\}\cup\{0,0\},$$

$$Sp(LC_r)=\{\pm\frac{1}{2}(\sqrt{9+8\cos\frac{2\pi j}{r}}\pm 1)\ |j=1,\ldots,r\}.$$

The spectrum of LC_r has been determined previously, but by a completely different (group theoretical) method [5].

4. The Matching Polynomial of G{K,H}

A statement which is fully analogous to Theorem 1 holds also for the matching polynomial of the graph G{K,H}.

Theorem 2:

$$\alpha(G\{K,H\})=[\alpha(H)/\alpha(K)]^{(b-a)/2}\ [\alpha(K^*)\alpha(H^*)]^{(a+b)/2}\ \cdot$$
$$\cdot\ \alpha(G,[\alpha(K)\alpha(H)/\alpha(K^*)\alpha(H^*)]^{1/2}) \qquad (13)$$

and

$$\alpha(G\{K,H\})=\ \alpha(H)^{b-a}\prod_{j=1}^{a}[\alpha(K)\alpha(H)-y_j{}^2\ \alpha(K^*)\alpha(H^*)]. \qquad (14)$$

Example: For the graphs $G\{L_1,L_2\}$ and $G\{L_2,L_1\}$ from Fig. 1 the application of Theorem 2 gives

$$\alpha(G\{L_1,L_2\})=(x^3-3x)[(x^4-3x^2)(x^3-3x)-4(x^3-2x)(x^2-1)]$$
$$[(x^4-3x^2)(x^3-3x)-(x^3-2x)(x^2-1)],$$

$\alpha(G\{L_2,L_1\})=(x^4-3x^2)[(x^4-3x^2)(x^3-3x)-4(x^3-2x)(x^2-1)]$
$[(x^4-3x^2)(x^3-3x)-(x^3-2x)(x^2-1)]$,

since $\alpha(L_1)=x^4-3x^2$, $\alpha(L_2)=x^3-3x$, $\alpha(L_1^*)=x^3-2x$, $\alpha(L_2^*)=x^2-1$ and

$$Sp_A(G)=\{2,1,0,-1,-2\}.$$

Proof: Theorem 2 can be proved by total induction. However, we shall not present this proof here, since just the same idea will be used in the subsequent paper [15] to obtain a more general result - Theorem 3.

Corollary 1: If K=H,

$$\alpha(G\{H\})=\alpha(H^*)^n \ \alpha(G,\alpha(H)/\alpha(H^*)), \tag{15}$$

$$\alpha(G\{H\})=\prod_{j=1}^{n} [\alpha(H)-y_j\alpha(H^*)]. \tag{16}$$

Eqs. (15) and (16) hold also for non-bipartite graphs.

Corollary 2: $Sp_A(G\{K,H\})$ contains at least b-a times the entire A-spectrum of H.

Corollary 3:

$$\alpha(G\{K,H\})\alpha(K)^{b-a} = \alpha(G\{H,K\})\alpha(H)^{b-a}.$$

In particular, if a=b, then the graphs G{K,H} and G{H,K} have equal matching polynomials for arbitrary K and H.

Using Theorem 2 we can determine the A-spectrum of several classes of graphs. As an example, for the previously considered molecular graphs $C_{2a}\{S_3,P_1\}$ and $C_{2a}\{S_4,P_1\}$ we obtain

$$Sp_A(C_{2a}\{S_3,P_1\}) = \{\pm[2\cos^2 \lambda_j \pm\sqrt{4\cos^4 \lambda_j + 1}]^{1/2} \mid j=1,\ldots,a\}, \quad (17)$$

$$Sp_A(C_{2a}\{S_4,P_1\}) = \{\pm\frac{\sqrt{2}}{2}[3+4\cos^2 \lambda_j \pm\sqrt{(3-4\cos^2 \lambda_j)^2 + 16\cos^2 \lambda_j}]^{1/2} \mid j =1,\ldots,a\} \cup \{0, \text{ a times}\}, \quad (18)$$

where $\lambda_j=\frac{(2j+1)\pi}{4a}$.

5. An Application:

Further Artifacts in the Topological Resonance Energy Method

Few years ago the topological resonance energy (TRE) was proposed as a theoretical index of aromaticity of conjugated molecules [16]. In spite of numerous successful applications, several intrinsic difficulties of the TRE method have been recently reported [17,18]. In particular, it was demonstrated [18] that a conjugated vinyl compound $R\text{-}CH{=}CH_2$ and the pertinent allyl radical $R\text{-}C(CH_2)_2$ (where R stays for an arbitrary conjugated substituent), have nearly equal TRE values, irrespective of their strikingly different chemical behaviour.

Using the results of the present paper, we can easily compute the TRE of s-vinyl- and s-allylannulenes. From (8), (9), (17) and (18) one can immediately calculate the numbers which are presented in Table 1.

Table 1

The TRE values (in β units) of s-vinyl[2a]annulenes and s-allyl[2a]annulene polyradicals

a	vinyl	allyl	difference
2	-0.941	-1.040	+0.099
3	+0.212	+0.233	-0.021
4	-0.432	-0.492	+0.059
5	+0.117	+0.132	-0.015
6	-0.282	-0.324	+0.041
7	+0.082	+0.093	-0.011

From Table 1 is seen that the TRE's of s-vinyl- and s-allylannulenes are nearly equal. Their difference is always smaller than 0.06β (except for a=2) and is thus negligible in chemical considerations. Therefore we may conclude that the TRE method cannot distinguish between relatively stable vinyl compounds and highly reactive, hypothetic and never synthetized allyl polyradical species. Furthermore, in the case of (4m)-annulenes, TRE predicts a higher aromaticity for the s-allyl species than for the s-vinyl molecule. These conclusions are in contradiction with experimental facts and are evidently artifacts of the TRE method.

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References

[1] For references about the early work on the solution of the HMO eigenvalue problem for particular classes of conjugated systems see: C.A. Coulson and A. Streitwieser, Dictionary of π-electron calculations, Pergamon Press, San Francisco 1965.

[2] For a full bibliography on the chemical and mathematical investigations on graph spectra see: D. Cvetković, M. Doob and H. Sachs, Spectra of graphs - theory and application, Academic Press, New York 1980.

[3] E. Heilbronner, Helv. Chim. Acta 37 (1954) 913; B.J. McClelland, J. Chem. Soc. Faraday II, 70 (1974) 1453.

[4] E. Heilbronner, Helv. Chim. Acta 37 (1954) 921.

[5] G. Derflinger and H. Sofer, Mh. Chem. 99 (1968) 1866.

[6] For some recent work on the application of symmetry arguments for the determination of the HMO eigenvalues see: G.G. Hall, Mol. Phys. 33 (1977) 551; S.S. D'Amato, Mol. Phys. 37 (1979) 1363; Theoret. Chim. Acta 53 (1979) 319.

[7] O.E. Polansky and N.N. Tyutyulkov, Match 3 (1977) 149, 225.

[8] M.V. Kaulgud and V.H. Chitgopkar, J. Chem. Soc. Faraday II, 73 (1977) 1385; 74 (1978) 951.

[9] I. Gutman, Publ. Inst. Math. (Beograd) 24 (1978) 53; Acta Chim. Acad. Sci. Hung. 99 (1979) 145.

[10] C.D. Godsil and B.D. McKay, Bull. Austral. Math. Soc. 18 (1978) 21.

[11] I. Gutman, Match 6 (1979) 75 and references therein.

[12] C.D. Godsil and I. Gutman, Z. Naturforsch. 34a (1979) 776.

[13] A.J. Schwenk in: R.Bari and F. Harary (Ed.), Graphs and combinatorics, Springer-Verlag, Berlin 1974, pp. 153-172.

[14] D.A. Bochvar, I.V. Stankevich and A.L. Chistyakov, Zh. Fiz. Khim. (U.S.S.R.) 35 (1961) 1337; 39 (1965) 1365; D.A. Bochvar and I.V. Stankevich, Zh. Fiz. Khim. (U.S.S.R.) 39 (1965) 2028, 40 (1966) 2626.

[15] I. Gutman and O.E. Polansky, Match, subsequent paper.

[16] I. Gutman, M. Milun and N. Trinajstić, Match 1 (1975) 171; J. Amer. Chem. Soc. 99 (1977) 1692; J. Aihara, J. Amer. Chem. Soc. 98 (1976) 2750.

[17] I. Gutman, Chem. Phys. Letters 66 (1979) 595; Theoret. Chim. Acta, in press.

[18] I. Gutman and B. Mohar, Chem. Phys. Letters 69 (1980) 375.