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A novel use of Hückel parameters (h, k) for the pairing of eigenvalues in graph spectrum

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An unusual use of the Hückel parameters (h and k) has been noticed for the derivation of the characteristic polynomial (CP) of the vertex-edge weighted graphs. A new pairing scheme for the eigenvalues (x_j) of the weighed graphs has been proposed in the light of Coulson-Rushbrooke pairing theorem for the non-bipartite graphs,

$$x_j + x_{n+1-j} = 1/2 \sum_p h_p \pm a \text{ for } j = 1, 2, 3 ..., n$$

where n, p and 'a' are the number of vertices, number of heteroatoms and a numerical quantity respectively.

According to Coulson-Rushbrooke pairing theorem[1] a graph without weighted edges and/or vertices is bipartite if and only if its spectrum, considered as a set of points on the real axis, is symmetric with respect to zero point. While analysing the graph spectrum of 1,3-diazacyclobutadiene, Cvetković *et al.*[2] have shown that the graph spectrum bears a single zero eigenvalue. They have explained that out of the two zeros (NBMOs), in cyclobutadiene system, one acquires a positive eigenvalue (HOMO) leading to the stability of the system. Trinajstić *et al.*[3,4] have extended Coulson-Rushbrooke pairing theorem as follows.

If G is a bipartite graph the same number of vertices in each set, and those in the first set are weighted, then

$$X_j + X_{n+1-j} = h \text{ for } 1 \le j \le n \qquad \dots (1)$$

where h is the Hückel parameter or the weight of the loop. This theorem happens to be a restricted extension of the original pairing theorem. Coulson[5] pointed out that the validity of the pairing theorem would not be affected by the presence of the weights on the edges. We would like to point out that changing the weight of the edge changes the mode of distribution of the weight of the loop (h) in different eigenvalues, but the sum of the eigenvalues remains same, i.e., h. For instance, the CP of the graph (ii) (see Fig. 1) can be represented as follows.

$$CP_{ii} = X^4 - (h_1 + h_2)X^3 + [h_1h_2 - 2(k_1^2 + k_2^2)]X^2 + (2h_1k_2^2 + 2h_2k_1^2)X \qquad \dots (2)$$

When X=Y=N, the accepted values[6] of k and h are 0.7 and 0.38 respectively. With these parameters the eigenvalues are found to be 1.6028, 0.3800, 0.0000 and −1.2228. By changing the k value only, (k=1) the eigenvalues obtained are 2.1990, 0.3800, 0.0000 and −1.8190. Considering these eigenvalues it can be concluded that the summation of all the eigenvalues would be unaffected (in conformity with Mallion *et al.*'s work[3]), but two eigenvalues would change. When X≠Y, it is not in conformity with Mallion *et al.*'s equation. We have made an attempt to formulate a new type of pairing theorem which can deal with both bipartite and non-bipartite graphs[7].

Theoretical

Trinajstić[4] has constructed the CP for the vertex-edge weighted graph and redesigned it as[8],

$$CP = \sum_{n=0}^{N} \sum_{s \varepsilon S_n} (-1)^{P(s)} 2^{r(s)} \prod_{i}^{s} h_i \prod_{j}^{k_2 \text{ in } s} \times k_j^2 \prod_{j}^{c \text{ in } s} k_j^2 \qquad \dots (3)$$

where

N = total number of vertices,
s = a Sachs graph
S_n = a set of all Sachs graphs with n vertices,
$P(s)$ = total number of components in s,
$r(s)$ = total number of rings (or cyclic components) in s,
h_i = weight of the i th vertex having a loop in s,
k_j = weight of the j th edge in k_2 (Complete graph),
$k_{j'}$ = weight of the j'th edge in C (cyclic graph).

In this equation the first product refers to the contribution from all the weighted vertices 'i' with weights h_i in s, whereas the second and third products refer to the contribution from all the weighted components in 's' and all the weighted edges in 'C' components of 's' respectively.

Earlier, different workers have investigated the topological properties of heteroconjugated molecules[3,4,8,11]. Gutman has made a series of contributions on the topological studies of the heteroconjugated molecules[11-15]. The method of calculation of the CP of the vertex weighted (weighted self loop) graphs has been proposed by many workers[9,11]. Dias[10] has made use of McClelland's factorisation rule and proposed the CP for the vertex-edge weighted graph having one and two heteroatoms. The derivation of the CP clearly shows the crucial role played by both the Hückel parameters (h and k) simultaneously. Here, we have tried to construct the CP for the heteroconjugated system in terms of h and k parameters. As proposed by Trinajstić[4], the weight of the edge of a pendent graph would be reflected as the square of the weight of the edge. Hence, the CP is constructed as a function of $(h+k^2)$ term in its ascending powers.

$$CP = h^0[f_0(x)] + (k^2)^0[f_1(x)] + h[f_2(x)] + k^2[f_3(x)] + h^2[f_4(x)] + 2hk^2[f_5(x)] + k^4[f_6(x)].... \quad \ldots (4)$$

$$= (h+k^2)^0 \left[\frac{h^0 f_0}{(h+k^2)}(x) + \frac{k^2}{(h+k^2)^0} f_1(x)\right] + (h+k^2)^1\left[\frac{h}{(h+k^2)} f_2(x) + \frac{k^2}{(h+k^2)^0} f_3(x)\right] + (h+k^2)^2\left[\frac{h^2}{(h+k^2)} f_4(x) + \frac{2hk^2 f_5}{(h+k^2)}(x) + \frac{k^4}{(h+k^2)^2} f_6(x)\right] + ...$$

$$= (h+k^2)g_0(x, h, k^2) + (h+k^2)g_1(x, h, k^2) + (h+k^2)^2 g_2(x, h, k^2) + ... \quad \ldots (5)$$

Thus, Eq. 5 clearly shows the importance of both the Hückel parameters in the construction of the CP.

It has been observed that the pairing theorem[1,5] holds good for the bipartite graphs having neither weighted edges nor weighted self-loops[13,15,16]. Further, Gutman[16] has explained the above fact through an even and odd function of the heteroconjugated molecule containing a single heteroatom[17]. An exceptional class of heteroconjugated system has been proposed, for which the original pairing theorem holds good[15].

Results

Analysing the extended form of the pairing theorem[3,4], we have noticed that the vertex-edge weighted graph is made bipartite by equally weighting the vertices present in a particular set. But, if a graph is non-bipartite then this extended form can not hold good. The original pairing theorem holds good for a vertex weighted graph (containing two vertices V_1 and V_2), if the symmetry equivalent vertices are weighted[16] as h and − h.

Here, in this work we have considered a single vertex-edge weighted graph and two unequally weighted vertices (which may or may not be symmetry equivalent vertices) graphs. We have considered the following graphs having four (4) vertices only (Fig. 1).

With a view to revisiting the Coulson-Rushbrooke pairing theorem and its extended form, the eigenvalues of some cyclic systems with four atoms (atoms may be exocyclic) having one or more heteroatoms are computed. By analysing the CP of the graphs and the eigenvalues some interesting results have been observed.

(i) The weight of the edge also plays a vital role in determining the eigenvalues as well as in the pairing process where the graph is not a bipartite one.

(ii) The eigenvalues can be paired by assuming a model equation (Eq. 6) for the graphs consid-

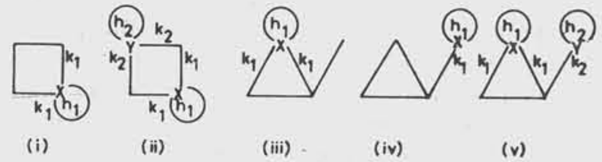

Fig. 1—Different graphs with four vertices where, X and Y are equal to N, P, As, Sb and Bi

Table 1—Eigenvalues, a, h_1, h_2, k_1 and k_2 values of the weighted graphs

Graph	X	Y	h_1	h_2	k_1	k_2	x_1	x_{-1}	x_2	x_{-2}	a
(i)	N		0.38		0.70		1.8006	−1.6729	0.2523	0.0000	0.0623
	P		0.30		0.67		1.7558	−1.6615	0.2057	0.0000	0.0557
	As		0.10		0.60		1.6631	−1.6366	0.0735	0.0000	0.0235
	Sb		−0.10		0.49		1.5657	−1.5851	0.0000	−0.0806	0.0306
	Bi		−0.10		0.40		1.5166	−1.5305	0.0000	−0.0861	0.0361
(ii)	N	N	0.38	0.38	0.70	0.70	1.6028	−1.2228	0.3800	0.0000	0.0000
	N	P	0.38	0.30	0.70	0.67	1.5525	−1.2105	0.3380	0.0000	0.0020
	N	As	0.38	0.10	0.70	0.60	1.4496	−1.1858	0.2162	0.0000	0.0238
	N	Sb	0.38	−0.10	0.70	0.49	1.3462	−1.1220	0.0559	0.0000	0.0841
	N	Bi	0.38	−0.10	0.70	0.40	1.2973	−1.0349	0.0176	0.0000	0.1224
	P	P	0.30	0.30	0.67	0.67	1.4983	−1.1982	0.3000	0.0000	0.0000
	P	As	0.30	0.10	0.67	0.60	1.3862	−1.1741	0.1879	0.0000	0.0121
	P	Sb	0.30	−0.10	0.67	0.49	1.2727	−1.1111	0.0384	0.0000	0.0616
	P	Bi	0.30	−0.10	0.67	0.40	1.2192	−1.0242	0.0050	0.0000	0.0950
	As	As	0.10	0.10	0.60	0.60	1.2510	−1.1510	0.1000	0.0000	0.0000
	As	Sb	0.10	−0.10	0.60	0.49	1.1098	−1.0900	0.0000	−0.0198	0.0198
	As	Bi	0.10	−0.10	0.60	0.40	1.0432	−1.0049	0.0000	−0.0382	0.0382
	Sb	Sb	−0.10	−0.10	0.49	0.49	0.9313	−1.0311	0.0000	−0.1002	0.0000
	Sb	Bi	−0.10	−0.10	0.49	0.40	0.8459	−0.9459	0.0000	−0.1000	0.0472
	Bi	Bi	−0.10	−0.10	0.40	0.40	0.7516	−0.8516	0.0000	−0.1000	0.0000
(iii)	N		0.38		0.70		2.0656	−1.5979	0.3439	−0.4316	0.2777
	P		0.30		0.67		2.0232	−1.6149	0.3204	−0.4287	0.2583
	As		0.10		0.60		1.9302	−1.6582	0.2602	−0.4322	0.2220
	Sb		−0.10		0.49		1.8321	−1.7123	0.1878	−0.4078	0.1698
	Bi		−0.10		0.40		1.7946	−1.7255	0.1579	−0.3270	0.1191
(iv)	N		0.38		0.70		2.1010	−1.2119	0.4909	−1.0	0.6991
	P		0.30		0.67		2.0884	−1.2052	0.4167	−1.0	0.7332
	As		0.10		0.60		2.0636	−1.1914	0.2277	−1.0	0.8222
	Sb		−0.10		0.49		2.0384	−1.1554	0.0170	−1.0	0.9330
	Bi		−0.10		0.40		2.0255	−1.1077	−0.0178	−1.0	0.9678
(v)	N	N	0.38	0.38	0.70	0.70	1.8844	−1.2567	0.2777	−0.1455	0.2477
	N	P	0.38	0.30	0.70	0.67	1.8603	−1.2393	0.2459	−0.1869	0.2810
	N	As	0.38	0.10	0.70	0.60	1.8096	−1.1876	0.1925	−0.3345	0.3820
	N	Sb	0.38	−0.10	0.70	0.49	1.7613	−1.0809	0.1488	−0.5492	0.5404
	N	Bi	0.38	−0.10	0.70	0.40	1.7467	−1.0322	0.1170	−0.5515	0.5745
	P	N	0.30	0.38	0.67	0.70	1.8264	−1.2530	0.2750	−0.1684	0.2334
	P	P	0.30	0.30	0.67	0.67	1.8011	−1.2361	0.2419	−0.2069	0.2650
	P	As	0.30	0.10	0.67	0.60	1.7480	−1.1861	0.1837	−0.3455	0.3619
	P	Sb	0.30	−0.10	0.67	0.49	1.6974	−1.0832	0.1362	−0.5504	0.5142
	P	Bi	0.30	−0.10	0.67	0.40	1.6816	−1.0349	0.1058	−0.5525	0.5467
	As	N	0.10	0.38	0.60	0.70	1.7005	−1.2455	0.2684	−0.2434	0.2150
	As	P	0.10	0.30	0.60	0.67	1.6721	−1.2296	0.2326	−0.2751	0.2425
	As	As	0.10	0.10	0.60	0.60	1.6131	−1.1831	0.1605	−0.3905	0.3300
	As	Sb	0.10	−0.10	0.60	0.49	1.5568	−1.0873	0.1000	−0.5695	0.4695
	As	Bi	0.10	−0.10	0.60	0.40	1.5381	−1.0398	0.0739	−0.5722	0.4983
	Sb	N	−0.10	0.38	0.49	0.70	1.5565	−1.2275	0.2619	-0.3109	0.1890
	Sb	P	−0.10	0.30	0.49	0.67	1.5242	−1.2139	0.2232	−0.3335	0.2103
	Sb	As	−0.10	0.10	0.49	0.60	1.4581	−1.1757	0.1348	−0.4172	0.2824
	Sb	Sb	−0.10	−0.10	0.49	0.49	1.3919	−1.0845	0.0766	−0.5841	0.4075
	Sb	Bi	−0.10	−0.10	0.49	0.40	1.3722	−1.0527	0.0354	−0.5549	0.4195
	Bi	N	−0.10	0.38	0.40	0.70	1.4788	−1.2071	0.2595	−0.2512	0.1317

Contd.

Table 1—Eigenvalues, a, h_1, h_2, k_1 and k_2 values of the weighted graphs—*Contd*

Graph	X	Y	h_1	h_2	k_1	k_2	x_1	x_{-1}	x_2	x_{-2}	a
	Bi	P	−0.10	0.30	0.40	0.67	1.4445	−1.1962	0.2197	−0.2681	0.1483
	Bi	As	−0.10	0.10	0.40	0.60	1.3747	−1.1674	0.1262	−0.3335	0.2075
	Bi	Sb	−0.10	−0.10	0.40	0.49	1.3084	−1.1087	0.0441	−0.4438	0.2997
	Bi	Bi	−0.10	−0.10	0.40	0.40	1.2832	−1.0662	0.0257	−0.4427	0.3170

ered in this work.

$$X_j + X_{n+1-j} = 1/2 \sum_p h_p \pm \text{ a where } 1 \le j \le n \quad \ldots (6)$$

p is the number of heteroatoms and n is the total number of vertices. Let us abbreviate $(n+1-j)$ as $-j$. Then one can write Eq. 6 as

$$X_j + X_{-j} = 1/2 \sum_p h_p \pm a \ldots (7)$$

Here 'a' is defined to be the distribution of Hückel parameters among the complementary eigenvalues. This term can be evaluated by solving the polynomial equation. (The derivation of 'a' has been presented in Appendix-A for two representative graphs). The 'a' values are given in Table 1. The analysis of 'a' values reveals the following results:

(a) In a heterocyclic system with one heteroatom, the 'a' value decreases with increasing atomic weight of the heteroatom in N family, when the heteroatom is in the ring.

(b) When the eteroatom is exocyclic, reverse is the case.

(c) When two heteroatoms are present in a heterocyclic system and both the heteroatoms are in the ring, the 'a' value will vanish for X = Y (graph ii). In case of fixed X and varying Y, the 'a' value will decrease with increasing atomic weight of Y. But when Y is exocyclic, reverse is the case.

(d) From Eq. 7, we obtain

$$(X_1 - X_2) + (X_{-1} - X_{-2}) = 2a \quad \ldots (8)$$

Each part of the LHS of Eq. 8 refers to the proximity of the orbitals. Hence, the 'a' value provides an idea of the amalgamation of the orbitals. With decreasing 'a' values the amalgamation of the orbitals increases leading to a fresh set of orbitals.

A new method has been proposed for the derivation of the CP for the vertex-edge weighted graph. The much celebrated pairing theorem has been extended for the non-bipartite graphs.

Appendix-A

For the graph (ii), the CP can be written as,

CP=

$$X^4 - (h_1 + h_2)X^3 + (h_1 h_2 - 2(k_1^2 + k_2^2))X^2 + (2h_1 k_2^2 + 2h_2 k_1^2)X$$

Using the solution for the cubic equation, one gets X_1, X_{-1} and X_2.

Now, $X_1 + X_{-1} = 1/2 \sum_p h_p = a$

and

$$X_2 + X_{-2} = 1/2 \sum_p h_p - a$$

or

$$X_j + X_{n+1-j} = 1/2 \sum_p h_p \pm \text{ a where } 1 \le j \le n.$$

$$|a| = 0.1666\,(h_1 + h_2) + 1.1547\, q^{1/2} \cos \frac{\pi + \phi}{3}$$

$$\phi = \cos^{-1}[3/q)^{3/2}\, r/2]$$

$$q = h_1 h_2 - 1/3\,(h_1 + h_2)^2 - 2(k_1^2 + k_2^2)$$

$$r = 2(h_1 k_2^2 + h_2 k_1^2) + (1/3)(h_1 + h_2)[h_1 h_2 - 2(k_1^2 + k_2^2)]$$
$$-(2/27)(h_1 + h_2)^3$$

For the graph (v), the CP can be expressed as a quartic equation of the following type.

$$CP = X^4 \text{-} (h_1 + h_2)X^3 + X^2(h_1 h_2 - 2k_1^2 - 2k_2^2 1)$$
$$+ X(h_1 + h_2 + h_1 k_2^2 + 2h_2 k_1^2 - 2k_1^2) + (k_1^2 k_2^2 - h_1 h_2)$$

The eigenvalues are paired by the above relation. |a| for this relation is given by,

$$|a| = [h^2 - 4(t - 4 - k^2)]^{1/2}/2$$

with,

$$t = z + (k^2 + 4)/3$$

$$z = (2/\sqrt{3})\, q_2^{1/2}\, [\cos(\Phi/3)]$$

$$\Phi = \cos^{-1}(3/q_2)^{3/2}\, r_2/2$$

$$q_2 = (k^4 + 32k^2 + 12h^2 + 16)/3$$

$$r_2 = (-2k^6 + 120k^4 + 480k^2 + 18h^2k^2 + 288h^2 - 128)/27$$

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