# Influence of the Hückel *k* Parameter on the Pairing of the Eigenvalues of Heteroconjugated Molecules†

Rama K. Mishra* and Swarna M. Patra

Chemical Physics Group, Department of Chemistry, Sambalpur University, Jyoti Vihar 768 019, India

Received September 18, 1996⊗

The net effect of a heteroatomic center (combined effect of *h* and *k* Hückel parameters) on the eigenvalues of certain heteroconjugated molecules is examined. The role of the *k* parameter is judged by comparing the eigenvalues of the vertex-weighted (self-loop) graphs with those of the vertex-edge-weighted graphs. The pairing of the eigenvalues for the above class of molecules is observed by using the original pairing theorem (Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193−200. Coulson, C. A.; Leary, B. O.; Mallion, R. B. *H*ückel *Theory for Organic Chemists*; Academic Press: London, 1978; pp 90−110), the restricted extension form of it (Mallion, R. B.; Schwenk, A. J.; Trinajstić, N. In *Recent Advances in Graph Theory*; Fiedler, M., Ed.; Academia: Prague, 1975; p 345. Trinajstić, N. *Croat. Chem. Acta* **1977**, *49* (4), 593−633), and a different pairing scheme proposed in this work. The newly proposed scheme for pairing of the eigenvalues for a monocyclic heteroconjugated system containing *n* atoms and having one or more heteroatoms can be written as $x_j + x_{n+1-j} = {}^1/_2(\Sigma_p h_p - b) \pm a$, where *p* is the number of heteroatoms, *a* is a numerical quantity, *b* contains few odd eigenvalues, and $1 \leq j \leq n$.

## INTRODUCTION

The graph theoretical version of the most celebrated Coulson−Rushbrooke pairing theorem[1] has been presented for a graph without weighted vertices and/or edges that is bipartite if and only if its spectrum, considered as a set of points on the real axis, is symmetric with respect to the zero point. Coulson et al.[2] have given mathematical proof of this famous three-part theorem. Here, we shall not broach the different aspects of the theorem and their proofs. An excellent treatment of the theorem can be found in the book by Coulson et al.[2] While proving the three different parts of the theorem, Coulson et al. have categorically mentioned that the theorem is valid for whatever numerical value may be assigned to $\beta$. Further, they have proved that the theorem would hold even if all the nonzero $H_{rs}$ matrix elements of the secular equation were not equal to the common value $\beta$ but were instead assigned different values for the different bonds. These workers have given the proof of the theorem for the alternant hydrocarbons (AHs). It has been observed that this theorem does not hold for the weighted systems having an alternant topology. Hence, a restricted extension of the theorem for the weighted system has been given.[3,4] But many workers[5] have shown the validity of the original theorem for the chemical species other than AHs. It is interesting to note that Gutman[6] has shown the validity of the original theorem for one exceptional class of heteroconjugated (weighted system) molecules. Since the validity of the pairing theorem has not been affected by the presence of weights on the edges, Gutman[6] has only considered the vertex-weighted (self-loop) graphs. While carrying out topological studies on the heteroconjugated molecules through a series of publications, Gutman[7] has nearly restricted his attention to the vertex-weighted graphs. Trinajstić et al.[3,4] have shown the validity of their restricted extension theorem by taking $H_{rs}$ or $k = 1$ for 1,3-diazacyclobutadiene and *s*-triazine.[4,8]

In this report, we revisit the original and the restricted extended pairing theorems for some heteroconjugated systems with variation of the *k* (Hückel) parameter. An attempt is made to show the role played by the *k* parameter for the pairing of the eigenvalues of some heteroconjugated molecules. In this report, the role of the *k* parameter is visualized through a different scheme for pairing of the eigenvalues.

## ROLE PLAYED BY THE *k* PARAMETER IN THE CHARACTERISTIC POLYNOMIAL (CP) OF $G_{VEW}$

Dias[9] has made use of McClelland's factorization rule[10,11] and proposed the CPs for the vertex-edge-weighted graphs ($G_{VEW}$) having one and two heteroatoms. The derivation of the CP clearly shows the crucial role played by both of the Hückel parameters (*h* and *k*). The CP is constructed by taking the *h* and *k* parameters. Trinajstić[8] has proposed that 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 the $(h + k^2)$ term (total heteroatomic character) in its ascending powers:

$$\mathrm{CP} = h^0[f_0(x)] + (k^2)^0[f_1(x)] + h[f_2(x)] + k^2[f_3(x)] + h^2[f_4(x)] + 2hk^2[f_5(x)] + k^4[f_6(x)] + \ldots \quad (1)$$

$$= (h + k^2)^0[A_0 f_0(x) + A_1 f_1(x)] + (h + k^2)^1[A_2 f_2(x) + A_3 f_3(x)] + (h + k^2)^2[A_4 f_4(x) + A_5 f_5(x) + A_6 f_6(x)] + \ldots \quad (2)$$

where $A_0 = h^0/(h + k^2)^0$, $A_1 = (k^2)^0/(h + k^2)^0$, $A_2 = h/(h + k^2)$, $A_3 = (k^2)/(h + k^2)$, etc., and $A_0 = A_1$.

$$\mathrm{CP} = (h + k^2)^0 g_0(x,h,k^2) + (h + k^2) g_1(x,h,k^2) + (h + k^2)^2 g_2(x,h,k^2) + \ldots \quad (3)$$

where $g_0(x,h,k^2) = A_0(f_0(x) + f_1(x))$, $g_1(x,h,k^2) = A_2 f_2(x) + A_3 f_3(x)$, and so on.

† Dedicated to Prof. M. Randić for his outstanding contributions to chemical graph theory.

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1997.

**Table 1.** Hückel Parameters ($h$ and $k$), Pairing of Eigenvalues, and $|a|$ of Some Heteroconjugated Systems

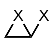
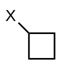
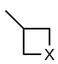
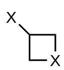
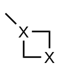
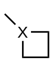
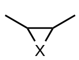
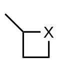
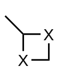
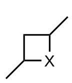
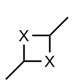
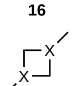
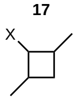
| graph no. | X | $h$ | $k$ | pairing of eigenvalues | eigenvalue pairs in $b$ | $\|a\|$ |
|---|---|---|---|---|---|---|
|  1 | N | 0.38 | 1.00 | $x_1 + x_4 = 0.191\ 70$<br>$x_2 + x_3 = 0.188\ 30$ | | 0.001 70 |
| | N | 0.38 | 0.70 | $x_1 + x_4 = 0.127\ 70$<br>$x_2 + x_3 = 0.252\ 31$ | | 0.062 31 |
|  2 | N | 0.38 | 1.00 | $x_1 + x_4 = 0.380\ 00$<br>$x_2 + x_3 = 0.380\ 00$ | | 0.000 000 |
| | N | 0.38 | 0.70 | $x_1 + x_4 = 0.380\ 00$<br>$x_2 + x_3 = 0.380\ 00$ | | 0.000 000 |
|  3 | N | 0.38 | 1.00 | $x_1 + x_4 = 0.826\ 92$<br>$x_2 + x_3 = -0.446\ 93$ | | 0.636 920 |
| | N | 0.38 | 0.70 | $x_1 + x_4 = 0.492\ 07$<br>$x_2 + x_3 = -0.112\ 06$ | | 0.302 070 |
|  4 | N | 0.38 | 1.00 | $x_1 + x_4 = 0.808\ 94$<br>$x_2 + x_3 = -0.428\ 93$ | | 0.618 940 |
| | N | 0.38 | 0.70 | $x_1 + x_4 = 0.889\ 12$<br>$x_2 + x_3 = -0.509\ 12$ | | 0.699 120 |
|  5 | N | 0.38 | 1.00 | $x_1 + x_4 = 0.942\ 61$<br>$x_2 + x_3 = -0.182\ 62$ | | 0.562 610 |
| | N | 0.38 | 0.70 | $x_1 + x_4 = 0.670\ 63$<br>$x_2 + x_3 = 0.089\ 37$ | | 0.290 630 |
|  6 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.053\ 25$<br>$x_2 + x_3 = 0.326\ 74$ | | 0.136 740 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.025\ 35$<br>$x_2 + x_4 = 0.354\ 65$ | | 0.164 650 |
|  7 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.145\ 94$<br>$x_2 + x_4 = 0.234\ 07$ | | 0.044 070 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.081\ 05$<br>$x_2 + x_4 = 0.298\ 95$ | | 0.108 950 |
|  8 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.196\ 95$<br>$x_2 + x_4 = 0.563\ 05$ | | 0.183 050 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.143\ 24$<br>$x_2 + x_4 = 0.616\ 76$ | | 0.236 760 |
|  9 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.380\ 00$<br>$x_2 + x_4 = 0.380\ 00$ | | 0.000 000 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.380\ 00$<br>$x_2 + x_4 = 0.380\ 00$ | | 0.000 000 |
|  10 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.237\ 17$<br>$x_2 + x_4 = 0.142\ 83$ | | 0.047 170 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.157\ 49$<br>$x_2 + x_4 = 0.222\ 51$ | | 0.032 510 |
|  11 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.786\ 04$<br>$x_2 + x_4 = -0.542\ 27$ | $x_3 = 0.136\ 23$ | 0.664 155 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.447\ 52$<br>$x_2 + x_4 = -0.273\ 80$ | $x_3 = 0.206\ 28$ | 0.360 660 |
|  12 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.165\ 81$<br>$x_2 + x_4 = 0.027\ 67$ | $x_3 = 0.186\ 51$ | 0.069 065 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.104\ 11$<br>$x_2 + x_4 = 0.026\ 70$ | $x_3 = 0.249\ 20$ | 0.038 710 |
|  13 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.470\ 79$<br>$x_2 + x_4 = -0.708\ 83$ | $x_3 = 0.618\ 03$ | 0.589 815 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.229\ 56$<br>$x_2 + x_4 = -0.505\ 01$ | $x_3 = 0.655\ 45$ | 0.367 285 |
|  14 | N | 0.38 | 1.00 | $x_1 + x_5 = 0.328\ 34$<br>$x_2 + x_4 = 0.051\ 66$ | $x_3 = 0.380\ 00$ | 0.138 340 |
| | N | 0.38 | 0.70 | $x_1 + x_5 = 0.273\ 92$<br>$x_2 + x_4 = 0.106\ 08$ | $x_3 = 0.380\ 00$ | 0.083 920 |
|  15 | N | 0.38 | 1.00 | $x_1 + x_6 = 0.153\ 57$<br>$x_3 + x_4 = 0.226\ 43$ | $x_2 + x_5 = 0.000\ 00$ | 0.036 430 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.095\ 51$<br>$x_3 + x_4 = 0.284\ 49$ | $x_2 + x_5 = 0.000\ 00$ | 0.094 490 |
|  16 | N | 0.38 | 1.00 | $x_1 + x_6 = 0.304\ 34$<br>$x_3 + x_4 = 0.455\ 65$ | $x_2 + x_5 = 0.000\ 00$ | 0.075 650 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.253\ 00$<br>$x_3 + x_4 = 0.507\ 00$ | $x_2 + x_5 = 0.000\ 00$ | 0.127 000 |
|  17 | N | 0.38 | 1.00 | $x_1 + x_6 = 0.380\ 00$<br>$x_3 + x_4 = 0.380\ 00$ | $x_2 + x_5 = 0.000\ 00$ | 0.000 000 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.380\ 00$<br>$x_3 + x_4 = 0.380\ 00$ | $x_2 + x_5 = 0.000\ 00$ | 0.000 000 |
|  18 | N | 0.38 | 1.00 | $x_1 + x_7 = 0.035\ 82$<br>$x_3 + x_5 = 0.344\ 18$ | $x_4 = 0.0$<br>$x_2 + x_6 = 0.0$ | 0.154 180 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.016\ 49$<br>$x_3 + x_5 = 0.363\ 51$ | $x_4 = 0.0$<br>$x_2 + x_6 = 0.0$ | 0.173 510 |

**Table 1** (Continued)

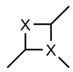
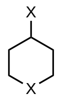
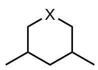
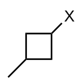
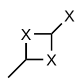
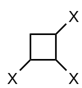
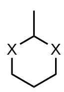
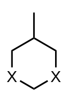
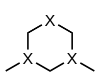
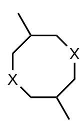
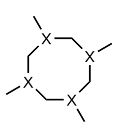
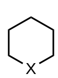
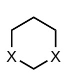
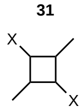
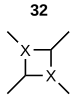
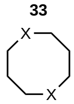
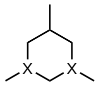
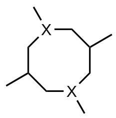
| graph no. | X | $h$ | $k$ | pairing of eigenvalues | eigenvalue pairs in $b$ | $\|a\|$ |
|---|---|---|---|---|---|---|
| <br>**19** | N | 0.38 | 1.00 | $x_1 + x_7 = 0.316\,88$<br>$x_3 + x_5 = 0.320\,30$ | $x_4 = 0.122\,86$<br>$x_2 + x_6 = 0.0$ | 0.001 730 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.267\,83$<br>$x_3 + x_5 = 0.309\,76$ | $x_4 = 0.182\,41$<br>$x_2 + x_6 = 0.0$ | 0.020 965 |
| <br>**20** | N | 0.38 | 1.00 | $x_1 + x_7 = 0.131\,29$<br>$x_2 + x_6 = 0.359\,34$ | $x_4 = 0.269\,37$<br>$x_3 + x_5 = 0.0$ | 0.114 025 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.075\,58$<br>$x_2 + x_6 = 0.370\,61$ | $x_4 = 0.315\,80$<br>$x_3 + x_5 = 0.0$ | 0.148 510 |
| <br>**21** | N | 0.38 | 1.00 | $x_1 + x_8 = 0.082\,97$<br>$x_3 + x_6 = 0.297\,03$ | $x_4 + x_5 = 0.0$<br>$x_2 + x_7 = 0.0$ | 0.107 030 |
| | N | 0.38 | 0.70 | $x_1 + x_8 = 0.032\,37$<br>$x_3 + x_6 = 0.347\,63$ | $x_4 + x_5 = 0.0$<br>$x_2 + x_7 = 0.0$ | 0.157 630 |
| <br>**22** | N | 0.38 | 1.00 | $x_1 + x_6 = 0.077\,43$<br>$x_3 + x_4 = 0.302\,58$ | $x_2 + x_5 = 0.380\,00$ | 0.112 580 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.042\,65$<br>$x_3 + x_4 = 0.337\,45$ | $x_2 + x_5 = 0.380\,00$ | 0.147 450 |
| <br>**23** | N | 0.38 | 1.00 | $x_1 + x_6 = 0.380\,00$<br>$x_3 + x_4 = 0.760\,00$ | $x_2 + x_5 = 0.380\,00$ | 0.190 000 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.380\,00$<br>$x_3 + x_4 = 0.760\,00$ | $x_2 + x_5 = 0.380\,00$ | 0.190 000 |
| <br>**24** | N | 0.38 | 1.00 | $x_1 + x_7 = 0.099\,56$<br>$x_3 + x_5 = 0.407\,20$ | $x_4 = 0.253\,25$<br>$x_2 + x_6 = 0.380\,00$ | 0.153 825 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.058\,35$<br>$x_3 + x_5 = 0.396\,56$ | $x_4 = 0.305\,10$<br>$x_2 + x_6 = 0.380\,00$ | 0.169 110 |
| <br>**25** | N | 0.38 | 1.00 | $x_1 + x_7 = 0.251\,73$<br>$x_2 + x_6 = 0.020\,51$ | $x_4 = 0.107\,76$<br>$x_3 + x_5 = 0.380\,00$ | 0.115 610 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.169\,08$<br>$x_2 + x_6 = 0.042\,57$ | $x_4 = 0.168\,36$<br>$x_3 + x_5 = 0.380\,00$ | 0.063 260 |
| <br>**26** | N | 0.38 | 1.00 | $x_1 + x_7 = 0.192\,36$<br>$x_2 + x_6 = 0.187\,64$ | $x_4 = 0.000\,00$<br>$x_3 + x_5 = 0.380\,00$ | 0.002 360 |
| | N | 0.38 | 0.70 | $x_1 + x_7 = 0.077\,48$<br>$x_2 + x_6 = 0.302\,53$ | $x_4 = 0.000\,00$<br>$x_3 + x_5 = 0.380\,00$ | 0.112 530 |
| <br>**27** | N | 0.38 | 1.00 | $x_1 + x_8 = 0.380\,00$<br>$x_3 + x_6 = 0.380\,00$ | $x_4 + x_5 = 0.000\,00$<br>$x_2 + x_7 = 0.380\,00$ | 0.000 000 |
| | N | 0.38 | 0.70 | $x_1 + x_8 = 0.380\,00$<br>$x_3 + x_6 = 0.379\,20$ | $x_4 + x_5 = 0.000\,00$<br>$x_2 + x_7 = 0.380\,00$ | 0.000 000 |
| <br>**28** | N | 0.38 | 1.00 | $x_1 + x_{10} = 0.145\,94$<br>$x_4 + x_7 = 0.234\,07$ | $x_3 + x_8 = 0.380\,00$<br>$x_5 + x_6 = 0.000\,00$<br>$x_2 + x_9 = 0.000\,00$ | 0.044 070 |
| | N | 0.38 | 0.70 | $x_1 + x_{10} = 0.081\,05$<br>$x_4 + x_7 = 0.298\,95$ | $x_3 + x_8 = 0.380\,00$<br>$x_5 + x_6 = 0.000\,00$<br>$x_2 + x_9 = 0.000\,00$ | 0.108 950 |
| <br>**29** | N | 0.38 | 1.00 | $x_2 + x_{11} = 0.380\,00$<br>$x_1 + x_{12} = 0.380\,00$ | $x_5 + x_8 = 0.000\,00$<br>$x_6 + x_7 = 0.000\,00$<br>$x_4 + x_9 = 0.380\,00$<br>$x_3 + x_{10} = 0.380\,00$ | 0.000 000 |
| | N | 0.38 | 0.70 | $x_2 + x_{11} = 0.380\,00$<br>$x_1 + x_{12} = 0.380\,00$ | $x_5 + x_8 = 0.000\,00$<br>$x_6 + x_7 = 0.000\,00$<br>$x_4 + x_9 = 0.380\,00$<br>$x_3 + x_{10} = 0.380\,00$ | 0.000 000 |
| <br>**30** | N | 0.38 | 1.00 | $x_1 + x_6 = 0.129\,81$<br>$x_2 + x_4 = 0.250\,19$ | $x_3 + x_5 = 0.000\,00$ | 0.060 190 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.056\,75$<br>$x_3 + x_4 = 0.323\,25$ | $x_2 + x_5 = 0.000\,00$ | 0.133 250 |
| <br>**31** | N | 0.38 | 1.00 | $x_1 + x_6 = 0.254\,22$<br>$x_3 + x_5 = 0.125\,78$ | $x_2 + x_4 = 0.380\,00$ | 0.064 220 |
| | N | 0.38 | 0.70 | $x_1 + x_6 = 0.145\,27$<br>$x_2 + x_5 = 0.234\,72$ | $x_3 + x_4 = 0.380\,00$ | 0.044 720 |
| <br>**32** | N | 0.38 | 1.00 | $x_1 + x_8 = 0.056\,72$<br>$x_4 + x_5 = 0.323\,28$ | $x_2 + x_6 = 0.380\,00$<br>$x_3 + x_7 = 0.000\,00$ | 0.133 280 |
| | N | 0.38 | 0.70 | $x_1 + x_8 = 0.029\,26$<br>$x_4 + x_5 = 0.350\,73$ | $x_2 + x_7 = 0.000\,00$<br>$x_3 + x_6 = 0.380\,00$ | 0.160 730 |
| <br>**33** | N | 0.38 | 1.00 | $x_1 + x_8 = 0.324\,50$<br>$x_4 + x_5 = 0.055\,50$ | $x_3 + x_7 = 0.000\,00$<br>$x_2 + x_6 = 0.380\,00$ | 0.134 500 |
| | N | 0.38 | 0.70 | $x_1 + x_8 = 0.278\,21$<br>$x_4 + x_5 = 0.101\,78$ | $x_2 + x_7 = 0.000\,00$<br>$x_3 + x_6 = 0.380\,00$ | 0.088 210 |
| <br>**34** | N | 0.38 | 1.00 | $x_1 + x_8 = 0.191\,70$<br>$x_4 + x_5 = 0.188\,30$ | $x_3 + x_7 = 0.000\,00$<br>$x_2 + x_6 = 0.380\,00$ | 0.001 700 |
| | N | 0.38 | 0.70 | $x_1 + x_8 = 0.127\,70$<br>$x_4 + x_5 = 0.252\,31$ | $x_2 + x_7 = 0.000\,00$<br>$x_3 + x_6 = 0.380\,00$ | 0.062 310 |

**Table 1** (Continued)

| graph no. | X | $h$ | $k$ | pairing of eigenvalues | eigenvalue pairs in $b$ | $\|a\|$ |
|---|---|---|---|---|---|---|
|  35 | N | 0.38 | 1.00 | $x_1 + x_9 = 0.253\,79$<br>$x_3 + x_8 = 0.126\,22$ | $x_2 + x_7 = 0.380\,00$<br>$x_4 + x_6 = 0.000\,00$<br>$x_5 = 0.000\,00$ | 0.063 790 |
| | N | 0.38 | 0.70 | $x_1 + x_9 = 0.106\,51$<br>$x_2 + x_8 = 0.273\,49$ | $x_3 + x_7 = 0.380\,00$<br>$x_4 + x_6 = 0.000\,00$<br>$x_5 = 0.000\,00$ | 0.083 490 |
|  36 | N | 0.38 | 1.00 | $x_1 + x_{12} = 0.191\,69$<br>$x_4 + x_9 = 0.188\,30$ | $x_3 + x_{11} = 0.0$<br>$x_5 + x_8 = 0.0$<br>$x_6 + x_7 = 0.0$<br>$x_2 + x_{10} = 0.38$ | 0.001 690 |
| | N | 0.38 | 0.70 | $x_1 + x_{12} = 0.101\,67$<br>$x_4 + x_9 = 0.278\,33$ | $x_3 + x_{10} = 0.380\,00$<br>$x_5 + x_8 = 0.000\,00$<br>$x_6 + x_7 = 0.000\,00$<br>$x_2 + x_{11} = 0.000\,00$ | 0.088 330 |

This equation shows the importance of both the $h$ and $k$ parameters. Further, it can be pointed out that whenever $h$ is there, logically the $k$ parameter is to be considered in order to distinguish C−X and C−C bonds. Also, we would like to point out that, in eqs 1−3, different heteroatoms can be considered as ($h_1$,$k_1$), ($h_2$,$k_2$), .... Following the above equations, the CPs of pyridine and pyrazine could be written as

$$\mathrm{CP(pyridine)} = (h + k^2)^0[A_0(X^6 - 4X^4 + 3X^2)] + (h + k^2)[A_2(-X^5 + 4X^3 - 3X) + A_3(-2X^4 + 6X^2 - 4)] \quad (4)$$

$$\mathrm{CP(pyrazine)} = (h + k^2)^0[A_0(X^6 - 2X^4 + X^2)] + (h + k^2)[A_2(-2X^5 + 4X^3 - 2X) + A_3(-4X^4 + 4X^2)] + (h + k^2)^2[A_4(X^4 - 2X^2 + 1) + A_5(2X^3 - 2X) + A_6(4X^2 - 4)] \quad (5)$$

Analyzing eq 3, one can say that $h$ and $k$ are necessary in order to characterize the effect of the heterocenter of the heteroconjugated molecules.

## ROLE OF THE $k$ PARAMETER ON THE EIGENVALUES OF THE $G_{VEW}$

Before analyzing the role of the $k$ parameter on the eigenvalues of the $G_{VEW}$, let us give a brief review of the mathematical picture of both pairing theorems (the original and its restricted extended form):

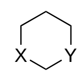
$$x_j + x_{n+1-j} = 0 \qquad \text{(original pairing theorem)} \quad (6)$$

$$x_j + x_{n+1-j} = h \qquad \text{(restricted extended theorem)} \quad (7)$$

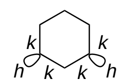
where $j$ = 1, 2, 3, 4, ..., $n$ (i.e., $1 \le j \le n$).

Here, $h$ is the weight of the loop, $n$ is the total number of atoms, and $x_1$, $x_2$, $x_3$, ..., $x_n$ are the eigenvalues of the molecular graph. In both of the above theorems, bipartite molecular graphs are considered. In the case of the restricted extended theorem, the atoms present in one set of a bipartite graph are weighted, and the theorem has been proved.

When one of the nitrogen atoms of the 1,3-diazacyclobutadiene is replaced by a phosphorus, arsenic, antimony, or bismuth atom, then eq 7 requires certain modifications. It is well known that the validity of the original pairing theorem will not be affected by the presence of the weights of the edges.[2] Here, we would like to point out that if the vertices are unweighted, then the above consideration is true. But, for the heteroconjugated molecule, the weight of the edges changes some of the eigenvalues, and thereby the pairing process can be affected. Let us consider a heteroconjugated molecule containing two heteroatoms:



six–membered heteroconjugated molecule



$G_{VEW}$

In the above graph, if X = Y = N, then the accepted values of $h$ and $k$ are 0.38 and 0.7, respectively.[12] With these $h$ and $k$ values, the eigenvalues obtained are 1.74916 ($x_1$), 0.961 40 ($x_2$), 0.915 33 ($x_3$), −0.535 33 ($x_4$), −0.726 68 ($x_5$), and −1.603 89 ($x_6$). Upon changing $k$ = 1 (or making it only vertex-weighted), the eigenvalues become 2.141 72, 1.207 89, 1.059 61, −0.827 89, −0.933 83 and −1.883 56, respectively. When X = Y = P, As, Sb, and Bi, the above change in the eigenvalues can also be observed with the accepted $h$ and $k$ values.[13] To explain the deviation in the pairing process of the eigenvalues, we propose the following two equations:

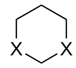
$$x_j + x_{n+1-j} = {}^1/_2\sum_p h_p \pm a \quad (8)$$

$$x_j + x_{n+1-j} = {}^1/_2\Big(\sum_p h_p - b\Big) \pm a \quad (9)$$

In both these above equations, $p$ refers to the number of heteroatoms, $a$ is a numerical quantity which depends on the $h$ and $k$ parameters (derivation of $a$ for two representative graphs is given in Appendix A), and $b$ contains the odd eigenvalues, which do not participate in the pairing process. However, some eigenvalues of $b$ are paired by eqs 6 and 7.

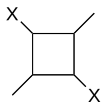
In this work, we have considered monocyclic heteroconjugated molecules (vertex-edge-weighted graphs) with total number of atoms equal to 4−12. The pairing of the eigenvalues of molecules **1**−**10**, **15**−**18**, **21**, and **30** (Table 1) obeys eq 8, whereas pairing of the eigenvalues of molecules **11**−**14**, **19**, **20**, **22**−**29**, and **31**−**36** obeys eq 9. The $a$ and $b$ values for the different molecules are also given in Table 1.

**Chart 1**



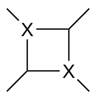

**31**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_1 + x_6$ = 0.254 22 | $x_1 + x_6$ = 0.145 27 |
| $x_2 + x_4$ = 0.380 00 | $x_2 + x_5$ = 0.234 72 |
| $x_3 + x_5$ = 0.125 78 | $x_3 + x_4$ = 0.380 00 |



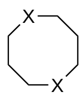

**32**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_1 + x_8$ = 0.056 72 | $x_1 + x_8$ = 0.029 26 |
| $x_2 + x_6$ = 0.380 00 | $x_2 + x_7$ = 0.000 00 |
| $x_3 + x_7$ = 0.000 00 | $x_3 + x_6$ = 0.380 00 |
| $x_4 + x_5$ = 0.323 28 | $x_4 + x_5$ = 0.350 73 |



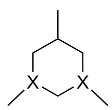

**33**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_1 + x_8$ = 0.324 50 | $x_1 + x_8$ = 0.278 21 |
| $x_2 + x_6$ = 0.380 00 | $x_2 + x_7$ = 0.000 00 |
| $x_3 + x_7$ = 0.000 00 | $x_3 + x_6$ = 0.380 00 |
| $x_4 + x_5$ = 0.055 50 | $x_4 + x_5$ = 0.101 78 |



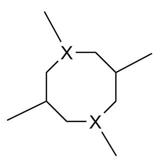

**34**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_1 + x_8$ = 0.191 7 | $x_1 + x_8$ = 0.127 70 |
| $x_2 + x_6$ = 0.380 0 | $x_2 + x_7$ = 0.000 00 |
| $x_3 + x_7$ = 0.000 0 | $x_3 + x_6$ = 0.380 00 |
| $x_4 + x_5$ = 0.188 3 | $x_4 + x_5$ = 0.252 31 |




**35**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_5$ = 0.000 00 | $x_5$ = 0.000 00 |
| $x_4 + x_6$ = 0.000 00 | $x_4 + x_6$ = 0.000 00 |
| $x_3 + x_8$ = 0.126 22 | $x_3 + x_7$ = 0.380 00 |
| $x_2 + x_7$ = 0.380 00 | $x_2 + x_8$ = 0.273 49 |
| $x_1 + x_9$ = 0.253 79 | $x_1 + x_9$ = 0.106 51 |




**3 6**

| $G_{VW}$ ($k$ = 1.0) | $G_{VEW}$ ($k$ = 0.7) |
|---|---|
| $x_6 + x_7$ = 0.000 00 | $x_6 + x_7$ = 0.000 00 |
| $x_5 + x_8$ = 0.000 00 | $x_5 + x_8$ = 0.000 00 |
| $x_4 + x_9$ = 0.188 3 | $x_4 + x_9$ = 0.278 33 |
| $x_3 + x_{11}$ = 0.000 0 | $x_3 + x_{10}$ = 0.380 00 |
| $x_2 + x_{10}$ = 0.380 0 | $x_2 + x_{11}$ = 0.000 00 |
| $x_1 + x_{12}$ = 0.191 69 | $x_1 + x_{12}$ = 0.016 7 |

## EFFECT OF THE $k$ PARAMETER ON THE EIGENVALUES AND ITS ROLE IN THE PAIRING PROCESS

The effect of $k$ on the eigenvalues and the role played by $k$ in the pairing process can be visualized by comparing a few vertex-weighted ($G_{VW}$, $h = 0.38$, $k = 1.0$) and vertex-edge-weighted ($G_{VEW}$, $h = 0.38$, $k = 0.7$) graphs. Let us examine the molecules **31**−**36** (Chart 1), with X = N. The complementary pairs are analyzed, and the pairing of the eigenvalues is examined.

The pairing of the eigenvalues for both cases (i.e., $G_{VEW}$ and $G_{VW}$, is explained by eq 9, and $|a|$ and $b$ values are also given for both cases (Table 1). The point we want to make is about the complementary pairs. When $k = 1$, the complementary pairs differ in the subscripts, as envisaged in the original and its restricted extended theorem. But, for $k = 0.7$, this deviation is rectified. Hence, molecules **31**−**36** can depict the role played by the $k$ parameter.

In this report, we have shown the total effect of the heterocenter (combined effect of $h$ and $k$ parameters) on the eigenvalues of the heteroconjugated molecules. The natural starting point of the study of eigenvalues is through the CP. A CP equation (eq 3) is developed to study the combined effect ($h$ and $k$) of the heterocenter in one additive form ($h + k^2$). A different pairing scheme of the eigenvalues is suggested in the form of eq 8. Equation 9 is a generalized form of eq 8. When analyzing the term $b$ in eq 9, we observed a deviation in $G_{VW}$ and $G_{VEW}$. A careful examination of the pairing process of the eigenvalues contained in $b$ of $G_{VW}$ and $G_{VEW}$ reveals the effect of the $k$ parameter in the pairing process in the above-studied heteroconjugated molecules.

(a)

(b)

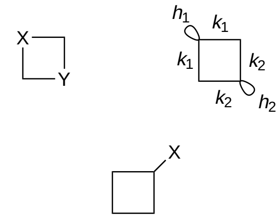



**Figure 1.** (a) Four-membered heteroconjugated molecule and its corresponding weighted graph. (b) Five-membered heteroconjugated molecular graph possessing a single heteroatom.

## ACKNOWLEDGMENT

S.M.P. thanks CSIR, New Delhi, India, for a Senior Research Fellow (SRF) position.

## APPENDIX A: DERIVATION OF $|A|$

Let us consider Figure 1a. The characteristic polynomial (CP) of the graph can be written as

$$\mathrm{CP} = X^4 - (h_1 + h_2)X^3 + [h_1h_2 - 2(k_1^{\,2} + k_2^{\,2})]X^2 + (2h_1k_2^{\,2} + 2h_2k_1^{\,2})X$$

Here, one of the eigenvalues is zero (i.e., $x_2 = 0$). Using the solution for the cubic equation, one gets $x_1$, $x_4$, and $x_3$.

Now, $x_1 + x_4 = {}^1/_2\Sigma_p h_p + a$, and $x_2 + x_3 = {}^1/_2\Sigma_p h_p - a$, or $x_j + x_{n+1-j} = {}^1/_2\Sigma_p h_p \pm a$, where $1 \le j \le n$.

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

where $\Phi = \cos^{-1}[(3/q)^{3/2}r/2]$, $q = h_1h_2 - {}^1/_3(h_1 + h_2)^2 - 2(k_1^2 + k_2^2)$, and $r = 2(h_1k_2^2 + h_2k_1^2) + {}^1/_3(h_1 + h_2)[h_1h_2 - 2(k_1^2 + k_2^2)]^{-22}/_7(h_1 + h_2)^3$.

Similarly, for the graph in Figure 1b, we can make use of a quartic polynomial, and the $|a|$ value can be obtained since $x_3 = 0$. The CP of the above graph can be written as follows:

$$\mathrm{CP} = X^5 - hX^4 - (4 + k^2)X^3 + 4hX^2 + 2k^2X$$

Using the solution of the quartic polynomial equation, one gets $x_1 + x_5 = {}^1/_2\sum_p h_p + a$, and $x_2 + x_4 = {}^1/_2\sum_p h_p - a$. Here,

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

where $t = z + (k^2 + 4)/3$, $z = (z/3^{1/2})q_2^{1/2}[\cos(\Phi/3)]$, $\Phi = \cos^{-1}(3/q_2)^{3/2}r_2/2$, $q_2 = (k^4 + 32k^2 + 12h^2 + 16)/3$, and $r_2 = (-2k^6 + 120k^4 + 480k^2 + 18h^2k^2 + 288h^2 - 128)/27$.

It may be noted that $|a|$ contains both $h$ and $k$ parameters.

**Supporting Information Available:** Test of eq 9 for X = P, As, Sb, and Bi (7 pages). Ordering information is given on any current masthead page.

## REFERENCES AND NOTES

(1) Coulson, C. A.; Rushbrooke, G. S. Note on the Method of Molecular Orbitals. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193−200.

(2) Coulson, C. A.; Leary, B. O.; Mallion, R. B. *Hückel Theory for Organic Chemists*; Academic Press: London, 1978; pp 90−110.

(3) Mallion, R. B.; Schwenk, A. J.; Trinajstić, N. In *Recent Advances in Graph Theory*; Fiedler, M., Ed.; Academia: Prague, 1975; p 345.

(4) Trinajstić, N. Computing the Characteristic Polynomial of a conjugated system using the Sachs Theorem. *Croat. Chem. Acta.* **1977**, *49* (4), 593−633.

(5) Gutman, I.; Mallion, R. B.; Rouvray, D. H. Extension of the pairing Theorem to Möbius Non-alternant Hydrocarbons. *J. Math. Chem.* **1991**, *8*, 355−366 (see also ref 5−10 therein).

(6) Gutman, I. Topological Studies on Heteroconjugated Molecules. *Z. Naturforsch.* **1984**, *399*, 152−154.

(7) Gutman, I. Topological studies on Heteroconjugated Molecules. VI. Alternant Systems with two heteroatoms. *Z. Naturforsch.* **1990**, *45a*, 1085−1089 (see also refs 1−4 therein).

(8) Trinajstić, N. *Chemical Graph Theory*, Vol. 1; CRC Press: Boca Raton, FL, 1983; p 76.

(9) Dias, J. R. *Molecular Orbital Calculations Using Chemical Graph Theory*; Springer Verlag: Berlin, 1993; pp 97−99.

(10) McClelland, B. J. Graphical Method for Factorising Secular Determinant of Hückel Molecular Orbital Theory. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1453−1456.

(11) McClelland, B. J. Eigenvalues of the Topological Matrix. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 911−916.

(12) Hess, B. A., Jr.; Schaad, L. J.; Holyoka, C. W., Jr. The Aromaticity of Heterocycles containing the Imine Nitrogen. *Tetrahedron* **1975**, *31*, 295−298.

(13) Ilić, P.; Sinković, B.; Trinajstić, N. Topological Resonance Energies of conjugated structures. *Isr. J. Chem.* **1980**, *20*, 258−269.

CI960053T