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Facile Determination of Molecular Graph Eigenvalues with Symmetrical Eigenvectors

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Abstract: Using an equation by Longuet-Higgins, a method for rapid determination of eigenvalues having symmetrical eigenvectors is illustrated. This equation was used to determine the points of singularity for the density of states for two frequently studied infinite conjugated benzenoid polymers.

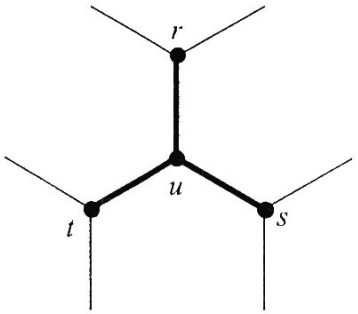
Introduction

Eigenvectors (HMO wave functions) of a molecular graph can be partially or fully deduced from the Coulson pairing theorem,[1] Hall subgraphs,[2] McClelland subgraphs,[3-4] the Longuet-Higgins equation,[5] Kassman's path deletion method,[6] and Mukherjee and Datta's vertex deletion method.[7] The purpose of this paper is to use Longuet-Higgins' equation to find the eigenvalues (HMO energy levels) that correspond to the symmetrical eigenvectors (those π orbitals eigenvectors with sets of coefficients that have the full symmetry of the graph, i.e. based on the totally symmetric adjacency eigenvectors). At this point, it is worthwhile to note the most positive eigenvalue will have an eigenvector with a single sign for all coefficients and consequently this eigenvalue will be among the eigenvalues having symmetrical eigenvectors.

We have previously[5] detailed an algorithm which uses the following equation by Longuet-Higgins (*cf.* with Figure 1) for determining the unnormalized eigenvector coefficients for a given eigenvalue X_i

$$-X_iC_{iu} + C_{ir} + C_{is} + C_{it} = 0.$$

C_{iu} is the eigenvector coefficient for some central (carbon) vertex u with adjacent vertices of r, s, and t. Herein, we show how to use this equation on symmetrical molecular graphs to determine the eigenvalues belonging to the symmetrical eigenvectors in a way that complements McClelland's mirror-plane fragmentation method.[4] McClelland's method identifies the eigenvalues belonging to the antisymmetric eigenvectors, and Hall's embedding method may identify eigenvalues belonging to either antisymmetric or symmetric eigenvectors, depending on the molecular graph. We will show how to use this algorithm on alternant two-fold and three-fold symmetrical molecular graphs in which the former includes linear polymers.



general vertex u

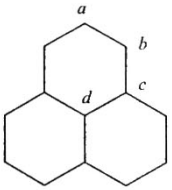
$$-X_i C_{iu} + C_{ir} + C_{is} + C_{it} = 0$$

Figure 1. The general relationship for any given molecular graph vertex u and its eigenvector coefficient C_{iu} for any ith eigenvalue X_i belonging to the molecular graph.

Results and Discussion

Phenalenyl monoradical and perylene

Our algorithm is most expeditiously performed on molecular graphs having sites that are equivalent by symmetry. The molecular graph of phenalenyl is representative of a three-fold symmetrical π–electronic system in which a $C_n = 2\pi/n = 120°$ rotation moves both starred and nonstarred carbon vertices into equivalent sites. In Figure 2, each symmetry distinct site is alphabetically labelled. Using the Longuet-Higgins equation on each of these four distinct sites gives four linear equations that can be solved for the symmetrical eigenvalues of phenalenyl monoradical. Previously, we showed that molecular graphs with greater than two-fold symmetry invariably had a doubly degenerate subset of eigenvalues.[8] For three-fold molecular graphs, two-thirds of the eigenvalues belong to the doubly degenerate subset and the other third are unique, except for accidental degeneracy (usually ±1 eigenvalues); odd carbon vertex-centric molecular graphs, like phenalenyl, have an extra (zero) eigenvalue. The doubly degenerate subset of eigenvalues for phenalenyl have been listed in our handbook.[9] Figure 2 shows that the unique eigenvalue subset of three-fold molecular graphs is given by our algorithm. It can be shown that phenalenyl can be embedded by pentalenyl three distinct ways, two them being mutually exclusive, resulting in the doubly degenerate eigenvalue subset consisting of the ±1, $\pm\sqrt{3}$ eigenvalues belonging to pentadienyl and having associated antisymmetric eigenvectors.



$$\begin{array}{l} -Xa + 2b = 0 \\ -Xb + a + c = 0 \\ -Xc + 2b + d = 0 \\ -Xd + 3c = 0 \end{array} \Longrightarrow \begin{array}{l} -Xa + 2b + 0 + 0 = 0 \\ a - Xb + c + 0 = 0 \\ 0 + 2b - Xc + d = 0 \\ 0 + 0 + 3c - Xd = 0 \end{array} \Longrightarrow \begin{vmatrix} -X & 2 & 0 & 0 \\ 1 & -X & 1 & 0 \\ 0 & 2 & -X & 1 \\ 0 & 0 & 3 & -X \end{vmatrix} = 0 = X^4 - 7X^2 + 6$$

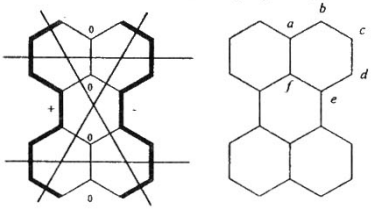
simultaneous equations | secular determinant | characteristic polynomial

$$X = \pm 1, \pm (6)^{1/2}$$

Unique eigenvalues having corresponding symmetric eigenvectors.

Figure 2. Determination of the eigenvalues having corresponding symmetric eigenvectors by using the algorithm in Figure 1.

Figure 3 shows perylene embedded in bold by 1,3,5,7-octatetraene (L_8). Also, shown are four selective lineations (lines) corresponding to four distinct ethene embeddings leading to four ±1 eigenvalue pairs; two pairs are antisymmetric (one already belonging to octatetraene embedding) and the other two symmetric. Thus, perylene has 10 antisymmetric eigenvectors. The second molecular graph in Figure 3 shows perylene only partially alphabetically labelled. These labelled sites are distinct but not in regard to a single symmetry axis like phenalenyl. To obtain all the eigenvalues having symmetrical eigenvectors without having to solve a 12×12 secular determinant, we will solve the 6×6 secular determinant shown (Figure 3) and use the pairing theorem for alternant molecular



perylene

L_8

$$\begin{array}{c} a \quad b \quad c \quad d \quad e \quad f \\ \begin{vmatrix} -X & 2 & 0 & 0 & 0 & 1 \\ 1 & -X & 1 & 0 & 0 & 0 \\ 0 & 1 & -X & 1 & 0 & 0 \\ 0 & 0 & 1 & -X & 1 & 0 \\ 0 & 0 & 0 & 1 & (1-X) & 1 \\ 1 & 0 & 0 & 0 & 2 & -X \end{vmatrix} \end{array} = X^6 - X^5 - 8X^4 + 5X^3 + 16X^2 - 4X - 9$$

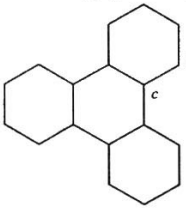
+2.5884
-2.1819
+1.5936
-1.0
+1.0
-1.0

Figure 3. Determination of the eigenvalues having corresponding symmetric eigenvectors by using the algorithm in Figure 1.

graphs to obtain the remaining ones. Small determinants of this size can be easily handled by the Laplace expansion method. Thus, perylene has 10 symmetric eigenvectors.

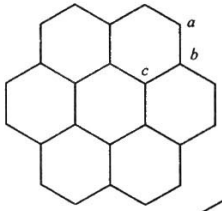
Three-fold molecular graphs

Figure 4 shows two molecular graphs corresponding to triphenylene (top) and tribenzo[*a,f,m*]coronene (bottom) with three-fold symmetry and the molecular graph of coronene (middle) with six-fold symmetry. To obtain the unique symmetric eigenvectors of the molecular graphs in Figure 4, we used the abbreviated method illustrated for perylene. Triphenylene ($C_{18}H_{12}$) has 6 unique eigenvalues corresponding to symmetric eigenvectors, coronene ($C_{24}H_{12}$) has 8, and tribenzocoronene ($C_{36}H_{18}$) has 12. In Figure 4 the unnormalized eigenvector coefficients are also given where the first coefficient (a = 1) was assigned the value of one. The doubly degenerate subset of eigenvalues for the molecular graphs in Figure 4 have been listed.[9-10]



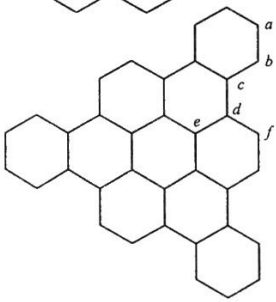
$-X^3 + 3X^2 - 3 = 0$

-0.8794; $a = 1$, $b = -1.8794$, $c = 0.6527$
1.3473; $a = 1$, $b = 0.3473$, $c = -0.5321$
2.5321; $a = 1$, $b = 1.5321$, $c = 2.8794$



$-X^3 + 3X^2 + X - 5 = 0$

-1.2143; $a = 1$, $b = -2.2143$, $c = 0.6888$
1.5392; $a = 1$, $b = 0.5392$, $c = -1.1701$
2.6751; $a = 1$, $b = 1.6751$, $c = 2.4811$



$X^6 - 5X^5 + 4X^4 + 12X^3 - 16X^2 - 4X + 8 = 0$

-1.41421; $a = 1$, $b = -2.41421$, $c = 2.41421$, $d = -3.41421$, $e = 1.0$, $f = 1.41421$
0.73205; $a = 1$, $b = -0.26795$, $c = -1.1962$, $d = -0.6077$, $e = -2.2679$, $f = -0.830$
1.0000; $a = 1$, $b = 0$, $c = -1$, $d = 0$, $e = 0$, $f = 1$
1.41421; $a = 1$, $b = 0.41421$, $c = -0.41421$, $d = -0.5858$, $e = 1.0$, $f = -1.41421$
2.0000; $a = 1$, $b = 1.0$, $c = 1.0$, $d = 0$, $e = -1.0$, $f = 0$
2.73205; $a = 1$, $b = 1.73205$, $c = 3.73205$, $d = 4.73205$, $e = 6.4641$, $f = 2.73205$

Figure 4. Unique eigenvalues having symmetric eigenvectors and their corresponding unnormalized coefficients.

Polymeric benzenoid strips

Hosoya and coworkers[11] have discussed the use and limitations of cyclic boundary conditions in the analysis of the infinite linear polymer systems given in Figure 5. They determined the density of states for a number of infinitely large polymeric benzenoid strips and showed that the energy levels of the cyclic dimer determined the singular points of their density of states.[11] Previously I showed that infinitely long polymer strips like polyacene (top molecular graph in Figure 5) could have their density of states determined by progressively embedding with increasing longer acenes (i.e., benzene, naphthalene, anthracene, tetracene, pentacene, etc.).[12] In this recursive process one could observe the growth the continuum of energy levels which ultimately formed the valence and conduction bands; in many cases, these could be projected after just a few progressive embedding iterations.

Polyacene and poly(perinaphthalene) in Figure 5 possess a plane of symmetry bisecting the strip into two sections. Poly(perinaphthalene) can be embedded by polyacetylene, and, thus, both polymers must have a zero band gap. Each naphthalene monomer (unit cell)of poly(perinaphthalene) can be embedded by ethene, an example of which is displayed at the right in Figure 5. This leads us to expect that the density of states for poly(perinaphthalene) will be particularly dense at the ±1 eigenvalues. For other studies which include these infinite polymers the reader should consult our prior work.[13]

The eigenvalue singular points for the density of states corresponding to symmetrical eigenvectors have been computed in Figure 5 for polyacene and poly(perinaphthalene) using the algorithm of Figure 1. Using an equivalent procedure, the singular points for the antisymmetric eigenvalues can be obtained; for polyacene they are 1.5616 and –2.5616 and for poly(perinaphthalene) they are 0 and 2.0000. Since the unit cell for polyacene contains only four carbon vertices, our algorithm has easily generated all the singular points of the density of states. However, the unit cell for poly(perinaphthalene) has ten vertices and our algorithm was truncated, as it was for perylene, to give 5 of the 10 singular points. We must use the pairing theorem to obtain the remaining 5 singular points.

While our results for poly(perinaphthalene) are in total agreement with the results of Hosoya and coworkers,[11] our results for polyacene differ in that the earlier workers also obtained the additional singular points of 0 and 1.0000. There are two fundamental differences between these two polymer strips that may be relevant. Polyacene ($C_{4n+2}H_{2n+4}$) can be constructed only by starting with an ethene seed structure (C_2H_4) and successively attaching the n 1,3-butadienetetrayl aufbau units (C_4H_2), whereas poly(naphthalene) ($C_{10n}H_{4n+4}$) has the same starting carbon skeleton seed structure and aufbau unit. This could suggest that some kind of end group effect is the cause.

In principle, the density of states interval can be open, closed, or half open. The open interval (a,b) determined by numbers a and b where $a < b$ is the set of all real numbers x such that $a < x < b$. The closed interval $[a,b]$ determined by a and b is the set of all real numbers x such that $a \leq x \leq b$. If just one of a or b is excluded from this closed interval, the resulting set of numbers is called the half-open interval, $[a,b)$ or $(a,b]$. The density of states interval for polyacene is bounded by (0,1] and for poly(naphthalene) by [0, 0.73205]. Perhaps, our algorithm can only determine the singular points to (fully) closed density of states intervals. Both of these differences appear to be related and are perhaps some type of end-group effect.

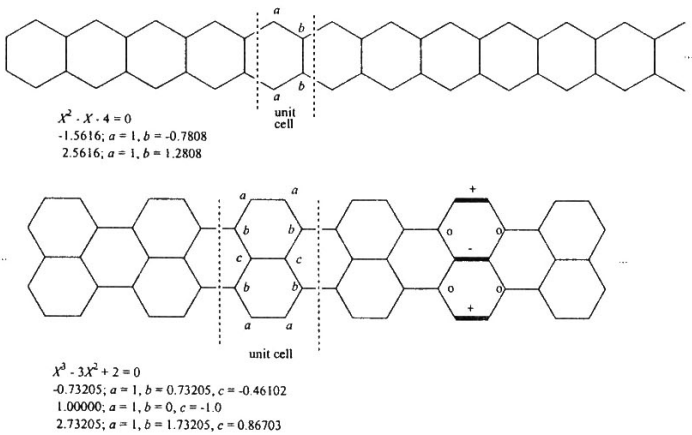


Figure 5. Polyacene and poly(perinaphthalene) benzenoid infinite polymer strips, respectively, and their symmetrical singular points of the density of states.

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