Evaluation of Level Pattern Indices

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A graphical approach is proposed for evaluating the level pattern indices (LPI) of conjugated molecules and clusters defined as a sequence of numbers of bonding, nonbonding, and antibonding molecular orbitals.

Level pattern indices (LPI) of molecules are defined as a sequence of numbers of bonding, nonbonding, and antibonding molecular orbitals symbolized by (n_+, n_0, n_-). In the Hückel framework, one knows that n_+, n_0, and n_- count respectively the positive, zero, and negative eigenvalues for the adjacency matrix of the molecule considered. It has been thought that LPI relates to the stability and valence state of the molecule,[1-6] for if $n_0 > 0$, it will be either a free radical or an unstable species with a minute HOMO–LUMO gap; on the other hand, if $n_0 = 0$ and $n_+ > n_-$ or $n_+ < n_-$, the ground state will exist as an anion or cation. Topics in relation to the non-Kekulean polyhexes[3,4] and non-alternants[7] having zero eigenvalues have been of interest so far. Early treatments on LPI were given by Gutman[5] that were based on the Descartes theorem of algebra to find a sequence of subgraphs and to evaluate the determinants of their adjacency matrices. Later on, Sinaloglu proposed the "structural covariance" method[6] which was generalized by Shen[8] furthermore. The principle of the present treatment is based on the Sylvester law of inertia of linear algebra,[9] in which the rank as well as the number of positive and negative coefficients in the diagonal forms of a real symmetric quadratic form are invariants with respect to real nonsingular transformations. It is clear that there is a biunique correspondence between quadratic forms and their matrices. Therefore, it is instructive to formulate the Sylvester law alternatively in terms of matrices instead of quadratic forms which has better feasibility for the evaluation of LPI of molecular graphs.

METHODOGY

Theorem. The rank as well as the number of positive and negative eigenvalues are invariants with respect to real nonsingular linear transformations.

P denotes the real matrix of transformation with nonzero determinant, with $\mathbf{P}^T$ being its transpose. Under this transformation, the symmetric matrix $\mathbf{A} = (a_{rm})$ is reduced to the block form, namely,

$$\mathbf{A} \rightarrow \mathbf{P}^T\mathbf{A}\mathbf{P} = \mathbf{A}_1 + \mathbf{A}_2 + \mathbf{A}_3 + \ldots + \mathbf{A}_s \qquad (1)$$

where $\mathbf{A}_j$ $(j = 1, 2, \ldots, s)$ represent submatrices; then LPI of **A** is equal to the sum of LPI of submatrices, i.e.

$$(n_+,n_0,n_-)_{\mathbf{A}} = \sum_{j=1}^{s}(n_+,n_0,n_-)_{\mathbf{A}_j} \qquad (2)$$

where the addition is carried out according to the definition of vectors, for example

$$(n_+)_{\mathbf{A}} = (n_+)_{\mathbf{A}_1} + (n_+)_{\mathbf{A}_2} + \ldots + (n_+)_{\mathbf{A}_s} \qquad (3)$$

It is obvious that the evaluation of LPI for smaller matrices is easier than larger ones, and eq 2 makes the calculation much more facile. Furthermore, in the Hückel framework, **A** represents adjacency matrices of molecular graphs with entries satisfying

$$a_{rm} = \begin{cases} 1, & \text{if r-atom is bonding to m-atom} \\ 0, & \text{otherwise} \\ a_{rm} \neq 1,\ a_{rr} \neq 0, & \text{if r is heteroatom} \end{cases} \qquad (4)$$

and meanwhile entries of submatrices $\mathbf{A}_j$ $(j = 1, \ldots, s)$ should be partly readjusted. Now, we use partition technique to attain the reduction of eq 1, and the procedure is appropriately formulated in terms of graphs in relationship to matrices.

The molecular graph is a collection of vertices (atoms) and edges (bonds) characterized by their weight with values determined by diagonal and off-diagonal entries according to eq 4. For carbon systems, vertices have weight 0 and edges have weight 1 which are always not labeled in the molecular graph; otherwise vertices and edges should be assigned specifically with their weights. Let's partition the adjacency matrix of graph G to the following block form[10,11]

$$\mathbf{A} = \mathbf{A}_G = \begin{bmatrix} \mathbf{A}_B & \mathbf{A}_{BC} \\ \mathbf{A}_{CB} & \mathbf{A}_C \end{bmatrix} \qquad (5)$$

where B and C signify two subgraphs (fragments) generated by erasing the edges connecting them; their adjacency matrices are denoted by $\mathbf{A}_B$ and $\mathbf{A}_C$, respectively. The off-diagonal blocks are rectangular in general and equal each other on transposition, specifying how B and C are connected in graph G. Take **P** to be

$$\mathbf{P} = \begin{bmatrix} \mathbf{I}_B & -\mathbf{A}_B^{-1}\mathbf{A}_{BC} \\ 0 & \mathbf{I}_C \end{bmatrix} \qquad (6)$$

where $\mathbf{I}_B$ and I_C represent identity blocks with dimensions similar to $\mathbf{A}_B$ and $\mathbf{A}_C$, respectively, 0 means zero block, and $\mathbf{A}_B^{-1}$ is the inverse of $\mathbf{A}_B$. On carrying out the multiplication of matrices, one can easily prove the following quality

$$\mathbf{P}^T\mathbf{A}\mathbf{P} = \begin{bmatrix} \mathbf{I}_B & 0 \\ -\mathbf{A}_{CB}\mathbf{A}_B^{-1} & \mathbf{I}_C \end{bmatrix}\begin{bmatrix} \mathbf{A}_B & \mathbf{A}_{BC} \\ \mathbf{A}_{CB} & \mathbf{A}_C \end{bmatrix}\begin{bmatrix} \mathbf{I}_B & -\mathbf{A}_B^{-1}\mathbf{A}_{BC} \\ 0 & \mathbf{I}_C \end{bmatrix} = \begin{bmatrix} \mathbf{A}_B & 0 \\ 0 & \mathbf{A}_{C'} \end{bmatrix} \qquad (7.1)$$

with

$$\mathbf{A}_{C'} = \mathbf{A}_C - \mathbf{A}_{CB}\mathbf{A}^{-1}\mathbf{A}_{BC} \qquad (7.2)$$

This illustrates the reduction of a symmetric matrix to the

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block form where $A_{C'}$ relates A_C via eq 7.2. This means, before testing, C is changed to C' by reweighting some of its vertices and edges. The details are as follows:

(1) If a vertex i in C is connected to B via t edges and there are r paths in B that include vertex i as a circuit, then, in C', the weight of the vertex i should be decreased by the value in accordance with formula 8, where ij denotes an erased

$$\{\sum_{j=1}^{t} a_{ij}^2 \det[A_{B-j}] + 2\sum_{c=c_1}^{C_r}(-1)^{Nc}\pi_c \det[A_{B-(c-i)}]\}/\det[A_B] \quad (8)$$

edge, c is a circuit, $c - i$ is the corresponding path left in B and π_c is the product of edge weights along circuit c, while $B-j$ and $B-(c-i)$ represent the fragments left after erasing vertex j and path $c - i$ in B, respectively, and N_c is the length of path c.

(2) If vertices i and k in C are simultaneously connected with B via erased edges and, in B, there were s paths with their ends linked to vertices i and k, respectively, then in C' the weight of edge ik is increased by the value of formula 9, where

$$\sum_{j\neq l} a_{ij}a_{kl}\sum_{p}(-1)^{Np}\pi_p \det[A_{B-p}]/\det[A_B] - \sum_{j} a_{ij}a_{kj} \det[A_{B-j}]/\det[A_B] \quad (9)$$

j and l denote the ends of two erased edges left in B, while $j = l$ means these two erased edges share a common vertex in B, and π_p is the product of edge weights along with p, N_p is the length of path p. Due to the sparse character of Hückel matrices, π_c, a_{ij}, etc. have value 1 or 0 mostly; thus formulas 8 and 9 often reduce to only a few terms, so it is simple in practice. The choices of B are important. It seems necessary to make

$$\det[A_B] \neq 0 \quad (10)$$

If B is an alternant fragment, then

$$\det[A_{B-j}] = 0 \quad (11)$$

so the first summation of formula 8 and the last summation in formula 9 disappear automatically. The remaining terms that involve $\det[A_{B-(c-i)}]$ and $\det[A_{B-p}]$ will be zero provided both circuit c is even and path p is odd. Take B to be a fragment of two vertices linked by edge jl; then formulas 8 and 9 are simplified as follows:

$$\frac{a_{ij}^2 a_{ll} + a_{il}^2 a_{jj}}{a_{jj}a_{ll} - a_{jl}^2} - 2\frac{a_{ij}a_{il}a_{jl}}{a_{jj}a_{ll} - a_{jl}^2} \quad (12)$$

$$\frac{a_{ij}a_{jl}a_{lk} + a_{il}a_{lj}a_{jk}}{a_{jj}a_{ll} - a_{jl}^2} + \frac{a_{il}a_{kl}a_{jj} + a_{ij}a_{jk}a_{ll}}{a_{jj}a_{ll} - a_{jl}^2} \quad (13)$$

If B is ethene-like, i.e. $a_{jj} = a_{ll} = 0$ and $a_{jl} = 1$, formulas 12 and 13 are furthermore reduced to

$$2a_{ij}a_{il}/a_{jl} \quad (14)$$

$$-(a_{ij}a_{lk} + a_{il}a_{jk})/a_{jl} \quad (15)$$

Such a reduction is displayed schematically in Figure 1, where the darkened part in C' includes two vertices and one edge that should be reweighted according to formulas 14 and 15, respectively.

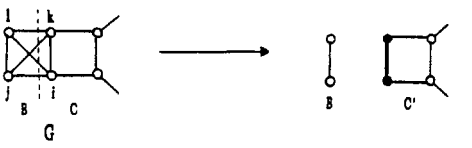

Figure 1. Partitioning of graph G with B being an ethene fragment.

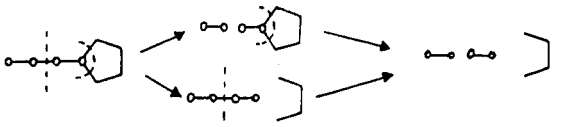

Figure 2. Partitioning of G: B = ethene and C' = C.

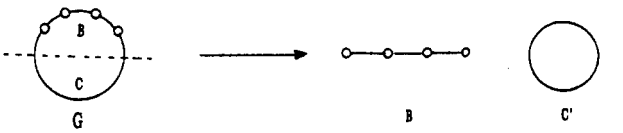

Figure 3. Partitioning of $(4n + m)$-membered circuit with B being a butadiene fragment.

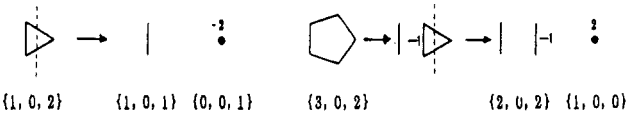

Figure 4. Partition modes for odd-membered circuits.

In a few special cases, $C' = C$ means no vertex and no edge needs reweighting; for example, on partitioning an ethene fragment from acyclic chains shown in Figure 2, one has such results. Apparently, LPI of graph G in Figure 2 is equal to the sum of LPI of two ethene and one butadiene fragments, namely, (4,0,4). On the other hand, one can verify that on partitioning a $(4n + m)$-membered circuit (m = 1, 2, or 3) in which B is a butadiene fragment, then C' becomes a $[4(n - 1) + m]$-membered circuit without reweighting, too. This is displayed in Figure 3. We have used dotted lines to indicate various partitions in Figures 1–3. The result displayed in Figure 3 reveals that LPI of $(4n + m)$-membered circuits with m fixed change regularly with respect to n; however, $n_+ - n_-$ and n_0 keep constant, respectively, independent of N. Therefore, it is valuable to use the sequence $[N, n_+ - n_-, n_0]$ to classify circuits.

APPLICATIONS

The theorem presented joint with partition technique to reduce the real symmetric matrices provides a tool for evaluating LPI for molecular graphs. We focus our attention on nonalternants, concealed non-Kekuleans, and clusters.

(1) Nonalternants. The simplest species of nonalternants are three-membered and five-membered circuits. We take the ethene fragment as B, carrying out their partitions via one and two steps, respectively, shown in Figure 4. By utilizing eqs 14 and 15, one determines that C' is a single vertex reweighted to –2 for the three-membered circuit and +2 for the five-membered circuit, giving one minus and one plus eigenvalues, and, as a consequence, their LPI are equal to (1,0,2) and (2,0,1), respectively. In Figure 4, LPI are tabulated below graphs G, B, and C' for clarity. Because $n_+ - n_-$ and n_0 remain unchanged on embedding a butadiene fragment into a circuit, thus one deduces that all $(4n + 3)$-circuits have $n_+ - n_- = -1$, i.e. one antibonding orbital more than bonding ones; on the contrary, there is one bonding species more than antibonding ones, since $n_+ - n_- = 1$ for all $(4n + 1)$-circuits.

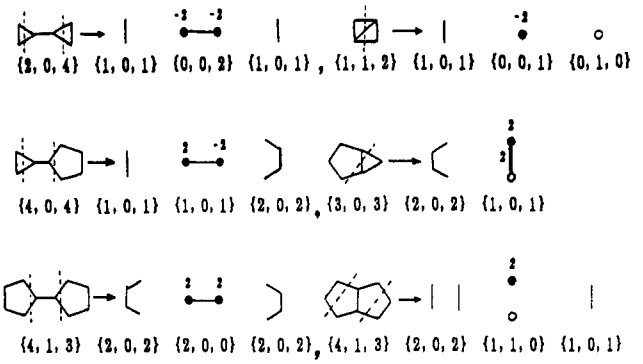

Figure 5. Schematic derivation of LPI for six nonalternants.

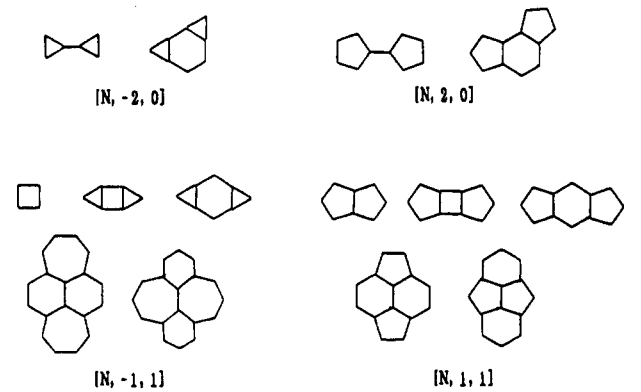

Figure 6. Nonalternants classified according to sequence $[N,n_+ n_-,n_0]$.

One can extend this treatment to nonalternants involving several odd-membered circuits. For illustration, the results of trifulvalene, calicene, fulvalene, etc. are given in Figure 5 which can be generalized in a similar way by embedding the butadiene fragment in each circuit respectively without altering the difference between the number of bonding and antibonding orbitals as well as $n_0 = 0$. Sometimes, it seems instructive to use sequence $[N,n_+ - n_-,n_0]$ instead of (n_+,n_0,n_-) to characterize molecular graphs. Most of nonalternant molecules are neutral with sequence $[N,0,0]$, but others that have $n_+ \neq n_-$ or $n_0 > 0$ may exist as ions or undergo distortions.[7] In Figure 6, a dozen of such molecular graphs are collected and classified in terms of sequence $[N,n_+ - n_-,n_0]$ which may be useful for some applications.[12]

(2) Non-Kekulean Polyhexes. Benzenoid hydrocarbons have nonbonding orbitals; $n_0 > 0$ can be partly recognized via a bicoloring procedure.[1-3] With the present method proposed, LPI can be readily derived for such species. Only two examples are given for illustration in Figure 7. In the first example, four terminal ethene fragments are elected as B, leaving $C' = C$ a pair of isolated vertices with normal weight, 0, so $n_0 = 2$. The second one is a concealed non-Kekulean in which one put B to be two anthracene fragments (see Figure 7) and $C' = C$ is valid, after carrying calculations according to both eqs 8 and 9. Both the LPI of anthracene and that of fragment C were known; therefore, LPI of this concealed non-Kekulean species is deduced by simple additions.

(3) Platonic Polyhedra. There are five species: tetrahedron, cube, octahedron, dodecahedron, and icosahedron together with their LPI given in Figure 8. For icosahedron, the partition can be started by taking two three-membered circuits along the 3-fold axis as B; then the C' obtained is further partitioned in succession such that the LPI of the fragments produced can be determined by inspection. The details of this procedure are displayed in Figure 8 for illustration.

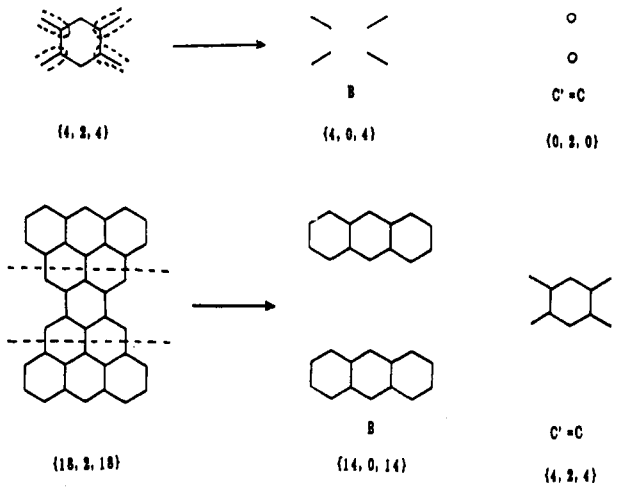

Figure 7. Partitioning of non-Kekulean graphs.

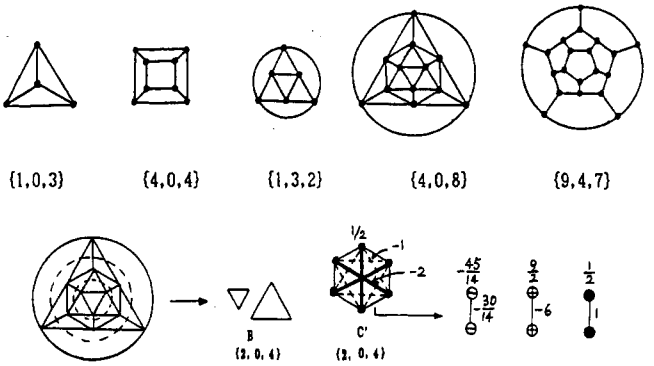

Figure 8. Platonic polyhedra and the partitioning of icosahedron.

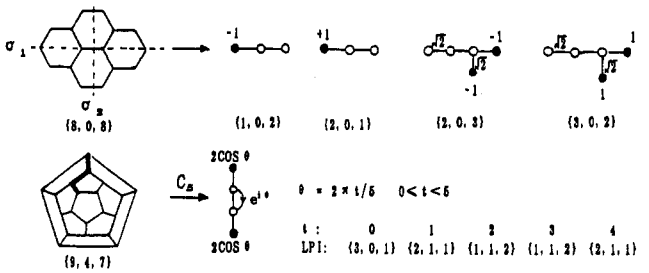

Figure 9. Evaluation of LPI of pyrene and dodecahedron via symmetry reduction.

USE OF SYMMETRY

Symmetry can be employed to simplify the evaluation of LPI too, where symmetry planes and n-fold axes are used quite often.[13,14] In Figure 9, two symmetry planes σ_1 and σ_2 are used to reduce the calculation of pyrene, while the 5-fold axis is used for symmetry reduction of dodecahedron, the heavy line shown in the graph represents a butadiene fragment used as the repeated unit for calculation.

As a final note, we have recently discovered a publication which presents an approach to LPI that has features very similar to the on espoused herein.[15]

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