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Minimally Kekulenoid π-Networks and Reactivity for Acyclics*

Douglas J. Klein and Anirban Misra**

Texas A&M University at Galveston, Galveston, Texas 77553, USA

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Graphs which admit exactly one Kekule structure are here termed »minimally Kekulenoid« and are suggested to be an interesting class of conjugated π-network structures, which then are investigated, especially for the alternant case. The inverses of the adjacency matrices of such molecular graphs are constructed, and found to represent a (generally edge-weighted) adjacency matrix of a »Kekulenoid transform« graph. These transforms are also studied, and a »multiplicative« pairing result is established for suitable circumstances. It is noted that tree graphs are either non-Kekulenoid or minimally Kekulenoid, and for the minimally Kekulenoid case the »Kekulenoid transform« are shown to be especially simple. Finally bounds for the HOMO-LUMO gap of tree graphs (representing acyclic conjugated polyenes) are obtained in terms of chemically appealing »conjugated-path« invariants. Some examples are presented, and some general chemical consequences relating to »cross conjugation« are identified.

INTRODUCTION

Mathematical chemistry has been formally recognized only during just the last few decades, with a strong influence involving graph theoretic work. This special influence is perhaps quite appropriate in view of its relevance in the classical core of chemistry, the characterization of molecular structure, and valence theory. Indeed the mathematical field of graph theory may be surmised to take its name from usage in chemistry. In particular J. J. Sylvester[1] in 1878 introduces the terminology of »graph« in mathematics in an article exuberantly reveling in the possible applications in chemistry where already the phrase »graphical representation« was in frequent use in describing the molecular structural formulas with which Sylvester was so deeply intrigued. Near simultaneously A. Cayley (who was a friend of Sylvester's) made[2] a notable application to enumeration of alkyl radicals and alkanes. But mathematical graph theory was not then well developed, and Sylvester's idea of a close interaction between mathematics and chemistry remained a dream, though there were a few isolated cases where Sylvester and Cayley's ideas were sought to be pursued.[3] Also in the mid 1930s G. Polya[4] further sought chemo-mathematical symbiosis, again through the use of graph theory, and ended up developing a mathematically fundamental combinatorial enumeration under group action, though again for a while the impact on chemistry was marginal. Starting in the 1930s E. Hückel, C. A. Coulson, and a host of other theoretical chemists developed a simple quantum mechanical »molecular-orbital« model of molecular electronic structure, which especially for conjugated π-networks entailed many graph-theoretically based ideas, though little inspiration was drawn from mathe-

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* Dedicated to Professor Nenad Trinajstić on the occasion of his 65th birthday, in recognition for his 30 years long fruitful research in Chemical Graph Theory.

** Author to whom correspondence should be addressed. (E-mail: kleind@tamug.edu) matical graph theory which was then but marginally developed, at least in the direction requisite for »molecular-orbital« chemical application. A similar situation applied for other areas of theoretical chemistry: *e.g.*, valence-bond theory (as championed by L. Pauling) and statistical mechanical modelling (as developed by J. Mayer) both involved graphs, but again without formal reference to mathematical graph theory. Now in the last few decades there have been a number of theoretically oriented chemists who have sought to exploit for chemical purposes the now better developed mathematical field of graph theory, with Milan Randić and Nenad Trinajstić being two such of the leading proponents. Notable in fostering the field is Trinajstić's[5] *Chemical Graph Theory*, though also both these researchers (along with their numerous collaborators) have carried out a great deal of fundamental chemical graph-theoretical research, and in wider generality have championed the field of »mathematical chemistry«.

Here application to neutral (homonuclear) conjugated π-networks is made, particularly to those networks which are »minimally Kekulenoid« in the sense of having but one Kekule structure. Examples of such species are indicated in Figure 1. Presumably these species are chemically stable, but having only a minimal number of Kekule structures, they do not exhibit »resonance« in the simple sense. Of course, these species should typically be more reactive than species which do exhibit resonance (around conjugated $4n$+2-circuits). But further such minimally Kekulenoid species certainly differ amongst themselves in stability and reactivity. Thence these minimally Kekulenoid species are the natural class of species to study so as to understand stability issues beyond that indicated by (the otherwise dominant) »conjugated circuits«. Surprisingly few researchers seem to have investigated the general class of minimally Kekulenoid π-networks – but not so surprisingly Randić and Trinajstić[6] have looked at this problem, for much the same reasons as expressed here, though they detail to some extent the earlier[7,8] »conjugated circuits« theory (which also has some rather interesting history[9]). In the present work these minimally Kekulenoid species are graph-theoretically characterized when alternant (or bipartite), and a set of theorems are developed to culminate for the special case of acyclic polyenes in a simple estimate (in the context of the Hückel model) for the lowest energy electronic excitation – namely the so-called HOMO-LUMO gap. Being the lowest excitation energy, this is a (well-recognized) characteristic for the rearrangeability of electrons, and more particularly for chemical reactivity.

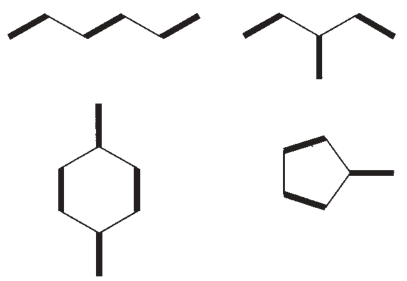

Figure 1. Four examplar minimally Kekulenoid species: 1,3,5-hexatriene, 3-methenyl-1,4-pentadiene, 1,4-dimethenylbenzene (or *para*-xylylene), and fulvene. The edges occurring in the unique Kekule structure (or perfect matching) are indicated in bold face.

This present endeavor is addressed in the standard mathematical format of definition/theorem/proof, but to be mathematical chemistry there should be some chemical relevance, and here some discussion is directed to this end. The overall mathematical approach to the so relevant HOMO-LUMO gap may be simply described: when non-singular, invert the adjacency matrix, whence the eigenvalues nearest 0 (as determine the HOMO-LUMO gap of bipartite graphs) become extremal (*i.e.* maximal or minimal), and thence are more readily susceptible to standard approximation techniques. A restriction of the considerations to alternants (bipartite graphs) facilitates the steps of non-singularity determination and matrix inversion, *via* methodology earlier considered,[10,11] and a further restriction to acyclic polyenes (Kekulenoid tree graphs) facilitates the final step of eigenvalue estimation, as earlier indicated.[12] Indeed some aspects of this general plan may be perceived in Godsil's work.[12] What seems at present the most chemically interesting results are embodied in the theorems A, B, N, O, P, and Q. A number of the intermediate results are proved in somewhat more generality than needed for these final results (of theorems N, O, P, and Q) but this greater generality may be more mathematically interesting. In such regard may be mentioned first ideas involving »Kekulenoid transforms« and second results concerning »multiplicative« eigenvalue pairing, such as seems in fact the emphasis of the paper[11] by Cvetković *et al.* Some of the pattern in these intermediate results seems suggestive of even further mathematically (or perhaps chemically) intriguing insights not yet proven, but which hopefully mathematical chemists (such as Nenad Trinajstić and Milan Randić) may enjoy investigating.

It is emphasized that the application of the HOMO-LUMO estimates (as in theorems N and P) may be made without the intermediate mathematical developmental results. That is, for a stronger chemical focus one might look at some of the graph-theoretic nomenclature in the next section, perhaps along with the statements of theorem A and proposition B (giving a neat way to identify minimally Kekulenoid graphs), then skip ahead first to the definitions of the invariants P_m along with the statements of the associated theorems N, P, and Q, and thereafter to the applications in the »examples« section and conclusion. In the conclusion some general chemical consequences with refernce to the topic of »cross conjugation« are presented in a less mathematical manner.

MINIMALLY KEKULENOID GRAPHS

Standard graph-theoretic notation is used, with a graph G specified by its set V(G) = V of vertices and its set E(G) = E of edges. Chemically G corresponds to a molecular structure, most simply of a hydrocarbon, with H atoms deleted (for the purposes of labeling). In the present paper all the hydrocarbons are conjugated so that the graph then just indicates the π network. A subgraph κ of G is termed a perfect matching if every vertex of G is a vertex of κ and is of degree 1 in κ. Evidently a perfect matching corresponds to a Kekule structure of G, with the edges of κ corresponding to double bonds, while other edges of G are single. Chemically a Kekule structure κ might be viewed as a »hypergraph« with double bonds strewn about superimposed on G, though in our mathematical work we view κ as a disjoint set of spanning edges of G (*i.e.* as a perfect matching). Graphs with at least one Kekule structure are termed Kekulenoid, those without a Kekule structure are termed non-Kekulenoid, and those with exactly one Kekule structure are termed minimally Kekulenoid.

It would be nice to characterize the minimally Kekulenoid graphs, or at least an important subset of them. A graph is bipartite (or alternant) if the vertices may be partitioned into two types starred ($\bigstar$) and unstarred ($\circ$) such that any site of one type has neighbors solely of the other type.

Theorem A. – Let G be a bipartite minimally Kekulenoid graph G. Then G must have at least one terminal (degree-1) starred vertex and at least one terminal unstarred vertex.

Proof: The problem of establishing the existence of an unstarred terminal vertex is first considered. Select a vertex i from the starred set $V_\bigstar$ of sites of G, and make it the first (and initially the only) member of an »examined« set $S_\bigstar$ of starred sites. Since by hypothesis G has one Kekule structure κ, i must be connected in this κ to a vertex i_o in the unstarred set $V_\circ$ of vertices. If i_o is terminal, then a terminal vertex in $V_\circ$ has been found, and otherwise select a vertex j connected to $i_\circ$ by an edge of G not in κ. Now $j \in V_\bigstar$ is not in $S_\bigstar$, so that j may be added to $S_\bigstar$ and j will be connected in κ to a new site $j_\circ \in V_\circ$. If $j_\circ$ is terminal, then a terminal vertex in $V_\circ$ has been found, and otherwise look for a vertex k to which $j_\circ$ is connected by an edge in G but not κ. If $k \in V_\bigstar$ were to be in the current examined set S, then we would have a conjugated circuit in hand and be able to make the alternative conjugation pattern around the cycle to generate a second Kekule structure, contrary to the theorem's hypothesis. Thus (if $j_\circ$ is not terminal) the newly selected vertex k not in the current $S_\bigstar$, may be added to $S_\bigstar$, and the site $k_\circ \in V_\circ$ to which k is connected in κ is selected. Again if $k_\circ$ is terminal, the goal of a terminal site in $V_\circ$ has been achieved, and otherwise a site l connected to $k_\circ$ in G but not in κ is selected. Again $l \in V_\bigstar$ is noted not to be in the current $S_\bigstar$ (again in order to avoid a conjugated circuit), and the whole process is iterated, till a terminal site in $V_\circ$ is found. If the process is iterated to the last site $z_\circ \in V_\circ$, then there is no site for it to connect back to (in $V_\bigstar$) and so it would necessarily be terminal. The existence of a terminal site in $V_\bigstar$ is similarly established (starting with an initial site i in $V_\circ$ rather than in $V_\bigstar$).

Evidently the restriction of theorem A to bipartite graphs is appropriate, since there are bipartite minimally Kekulenoid graphs with just one end (as fulvene in Figure 1) or with no ends (as in Figure 2). Further the occurrence of both $\bigstar$ and $\circ$ termini is necessary but not sufficient for a bipartite graph to be minimally Kekulenoid. A method to determine whether a graph (with termini) is minimally Kekulenoid should be of use. To this end we consider:

Kekulenoid-Test Algorithm. – Given a graph G with at least one terminus, »recur from the termini« by deleting a terminal vertex and its adjacent vertex to obtain a new graph G′ which then is subjected to further recursion *via* this algorithm.

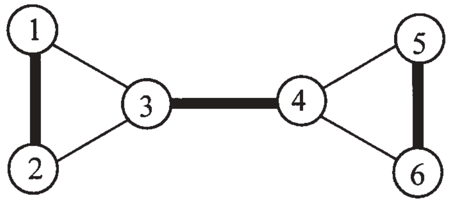

Figure 2. A site-numbering for an example nonbipartite (or nonalternant) minimally Kekulenoid species, which also has no terminal vertices.

For a general graph this algorithm might produce isolated sites or fragments without terminal sites (*e.g.*, cycles). But sometimes the algorithm iterates to eliminate all the sites, leaving at completion the empty graph.

Proposition B. – If for a graph G this algorithm continues to completion to yield the empty graph, then G is minimally Kekulenoid, and the pairs of vertices deleted in the algorithm identify the unique Kekule structure of G. Moreover if G is a minimally Kekulenoid bipartite graph, then this algorithm necessarily completes.

Proof: In the algorithm one starts at a terminal vertex i, say in $V_\bigstar$ connected to $i_\circ \in V_\circ$, and recognizes that if G is to have a Kekule structure κ, then i (being a terminus) must have the same edge $\{i, i_\circ\}$ in κ as in G. Then in eliminating i and $i_\circ$ from G, one is left with a new graph G′ which must have exactly one Kekule structure if G is to have one. Clearly, finally reaching the empty graph has identified G as minimally Kekulenoid. Further if G is bipartite, then if G is to turn out to be minimally Kekulenoid it must have termini, whence also G′ is minimally Kekulenoid and bipartite, so that the process necessarily goes to completion with the empty graph.

Thus this algorithm provides an efficient (order ~N) method by which to determine whether or not a bipartite graph G has a unique Kekule structure κ, indeed constructively giving this κ (if this G is so minimally Kekulenoid). Moreover the approach works on some non-alternant species, such as fulvene (in Figure 1), but not others (as that of the bicyclo species in Figure 2). Yet further the algorithm may be straight-forwardly modified[13] to test for (not necessarily minimal) Kekulenoidicity for general graphs.

The adjacency matrix $\mathbb{A}(G) = \mathbb{A}$ of a graph G has rows and columns in correspondence with the vertices, such that the only non-zero elements occur for positions i, j (and j,i) for $\{i, j\}\in E$ whence such an element is 1. Within the context of the Hückel model such an adjacency matrix gives (up to a scalar multiple and an additive shift) the molecular-orbital (MO) Hamiltonian matrix for a conjugated π-electron network.

Theorem C. – If G is an N-site minimally Kekulenoid bipartite graph, then det $\mathbb{A} = (-1)^{N/2}$.

Proof: This result is fairly readily seen *via* an old result of Sachs[14] which gives det $\mathbb{A}$ for a general graph in terms of spanning subgraphs with components which are either cycles or isolated edges. [Indeed Sachs' theorem goes on to similarly characterize all coefficients of the secular polynomial associated to $\mathbb{A}$; and much of what we presently need is also found in independent works by other authors, somewhat as indicated on page 36 of Ref. 15]. To prove the present result without recourse to Sachs work note that minimally Kekulenoid bipartite G may contain one or more cycles, but for our present case, what disjointly remains after deleting one such cycle does not admit a Kekule structure – for with pairs of alternating (or conjugated) patterns possible around such a deleted (necessarily even) cycle, there would then be more than one Kekule structure (contrary to hypothesis).

A tree is defined to be a connected acyclic graph, and is characterized by the fact that between any pair of vertices $i, j\in V$ there is a unique path.

Corollary D. – An N-site tree has either 0 or 1 Kekule structures (whence respectively either det$\mathbb{A}$ = 0 or det$\mathbb{A}$ = $(-1)^{N/2}$).

This is (essentially) also established in Ref. 11. The algorithm of proposition B along with theorem C then give a ready criterion by which to judge whether an alternant is minimally Kekulenoid or not, and granted this, then whether det$\mathbb{A}$ is 0 or not, and correspondingly whether $\mathbb{A}$ is singular or not. In particular, the adjacency matrix $\mathbb{A}$ for a tree T has an inverse if and only if T has a Kekule structure (or perfect matching). Thence we proceed with consideration of the non-singular case.

MATRIX INVERSION AND GRAPH PATHS

Some results leading toward matrix inversion for such as a graph's adjacency matrix is now to be considered. Given a matrix $\mathbb{M}$ and sets a and b of row and column labels, let $\mathbb{M}_{(a|b)}$ denote the matrix obtained upon deletion of the rows of a and the columns of b. For $n, m \in V$ let $\mathbb{M}'_{(n|m)}$ denote the matrix obtained from $\mathbb{M}$ by setting all elements in row n and column m to 0 except the (n,m)th which is set =1.

Lemma E. – Let $\mathbb{M}$ be an $N\times N$ matrix with non-zero elements outside the diagonal confined to positions (i, j) corresponding to edges $\{i, j\}$ of a graph G. Then

$$\det \mathbb{M}'_{(n|m)} = \sum_{\pi}^{m\to n} (-1)^{l(\pi)}\, M_{ab}\cdot M_{bc}\cdot\ldots\cdot M_{yz}\cdot \det \mathbb{M}_{(\pi|\pi)}$$

where the sum is over paths $\pi = (a,b,c,d,...,y,z)$ in G directed from m to n (*i.e.*, $m = a$ and $z = n$), and $l(\pi)$ is the length of the path π.

Proof: The proof follows somewhat an earlier one[10] formulated for the case that G is a tree, though much of the idea is implicit in even earlier work (involving tracing out permutative cyclic »paths« in determinants, *e.g.*, as in Sachs work in Ref. 14). For the determinant of $\mathbb{M}'_{(n|m)} \equiv \mathbb{M}'$

$$\det \mathbb{M}' = \textstyle\sum_P (-1)^P \prod_k (\mathbb{M}')_{k,P(k)}$$

where the sum is over all N! permutations P of indices of V, $(-1)^P$ is the parity of P, and P(k) is the image of $k\in V$ under P. But each term (identified by a P) is associated to a set of disjoint cycles, with each cycle contributing a separate factor, as

$$\pm(\mathbb{M}')_{ab}(\mathbb{M}')_{bc}\cdot\ldots\cdot(\mathbb{M}')_{xy}(\mathbb{M}')_{yz}\,(\mathbb{M}')_{za}$$

for the cycle of P which carries $a\to b\to c\to\ldots\to y\to z\to a$, and the ± sign depends on the parity of the cycle, which is − for a cycle of an even number of members and + for an odd number of members. For det $\mathbb{M}'_{(n|m)}$ the non-zero terms must evidently entail a cyclic permutation sending $m\to n$, and the remaining portion of such a cycle may be viewed as a path π from n to m. At the same time the other disjoint cycles simply build up the determinant for the portion of $\mathbb{M}'$ remaining after deletion of the rows and columns corresponding to the sites of π. Further the parity of the cycle moving $m\to n$ is just the length $l(\pi)$ of this path π. Thence one has

$$\det \mathbb{M}' = \sum_{\pi}^{m\to n} (-1)^{l(\pi)}\, (M')_{ab}\cdot(M')_{bc}\cdot\ldots\cdot(M')_{yz}\cdot 1\cdot \det \mathbb{M}_{(\pi|\pi)}$$

Further det $\mathbb{M}'$ is just that part of det $\mathbb{M}$ for permutations P which carry $m\to n$, except that the factor M_{mn} is missing. Anyway the lemma is proved.

A (self-avoiding) path in a Kekulenoid graph G is called a conjugated path with respect to a given Kekule structure κ if the path has its own Kekule structure which is a subgraph of κ. Indeed this definition coincides with that of Randić and Trinjastić,[6] though they term them »conjugated chains«. For minimally Kekulenoid graphs the particular Kekule structure κ is naturally understood. The number of disjoint edges (*i.e.*, of double bonds) in the Kekule structure of a conjugated path γ is denoted $k(\gamma)$, and thence is just half the (necessarily even) number of sites of γ. As an example, with the vertex numbering for the minimally Kekulenoid bicyclohexatriene of Figure 2, there are 3, 4, and 4 conjugated paths of different lengths

$k(\gamma) = 1$: (1,2), (3,4), (5,6)
$k(\gamma) = 2$: (1,2,3,4), (2,1,3,4), (6,5,4,3), (5,6,4,3)
$k(\gamma) = 3$: (1,2,3,4,5,6), (1,2,3,4,6,5), (2,1,3,4,5,6), (2,1,3,6,5)

With these definitions in hand, the result of lemma E can be specialized to

Lemma F. – Let $\mathbb{A}$ be the adjacency matrix of a minimally Kekulenoid bipartite graph. Then

$$\det \mathbb{A}'_{(i|j)} = -(-1)^{N/2} \sum_{\gamma}^{\mathrm{cp}:i,j} (-1)^{\,k(\gamma)}$$

where the sum is over all conjugated paths γ between i and j.

Proof: Here the restriction from the expression in lemma E to paths π which are conjugated paths occurs because of conditions for the remnant part det $\mathbb{M}_{(\pi|\pi)}$ to be non-zero (when $\mathbb{M} = \mathbb{A}$). In particular for a term associated with a permutation P in this remnant part to be non-zero, the permutation P could not involve any 1-cycles since all diagonal elements of $\mathbb{A}$ are 0. Nor could it involve any odd cycles because G is bipartite. As a consequence only even cycles (including possibly 2-cycles) could remain, thereby implying that the path π must have an even number of sites, and have a Kekule structure κ_π on the path π. But for such a contributing permutation P there is associated at least one Kekule structure $\kappa_{(\pi)}$ on the part of G remaining after deletion of all the sites of π: that is, each transposition (2-cycle) of P would locate an edge of such a Kekule structure, and any higher even cycle would if present allow 2 manners of conjugation around the cycle. But G being minimally Kekulenoid such higher cycles do not occur in the part of G outside of π. Then combination of κ_π and $\kappa_{(\pi)}$ together yields an overall Kekule structure κ which evidently must be the unique one (since G is minimally Kekulenoid). In particular this implies that κ_π is a subgraph of κ. The phase associated with a conjugated path γ is (from lemma E) just -1 to a power which is the length $l(\pi)$ of π, which is odd (for κ_π to occur). Now $\mathbb{A}_{(\pi|\pi)}$ is still the form of an adjacency matrix for a minimally Kekulenoid bipartite graph with $N-l(\pi)-1$ vertices, so that by corollary D one has det $\mathbb{A}_{(\pi|\pi)} = (-1)^{[N-l(\pi)-1]/2}$. Thus noting that $k(\pi) = [l(\pi)+1]/2$ it is seen that overall a phase $(-1)^{N/2}(-1)^{k(\pi)}$ occurs, and the proof is completed.

Now the well-known (Cramer's rule) result that

$$\det(\mathbb{A}^{-1})_{ij} = \det \mathbb{A}'_{(j|i)} \,/\, (\det \mathbb{A})$$

along with corollary D, then leads directly to:

Corollary G. – Let $\mathbb{A}$ be the adjacency matrix of a minimally Kekulenoid bipartite graph. Then $(\mathbb{A}^{-1})_{ij} = 0$ unless there is a conjugated path between i and j, whence

$$(\mathbb{A}^{-1})_{ij} = -\sum_{\gamma}^{\mathrm{cp}:i,j} (-1)^{\,k(\gamma)}$$

where the sum is over conjugated paths between i and j.

This result, which has also been established in Cvetković *et al.*[11] for the case of trees, and in (even in a somewhat more general manner) in Ref. 10. This result can be neatly rephrased if one describes the effective number of conjugated paths between two points i and j as the difference between those with numbers of sites being odd or even multiples of 2 (*i.e.*, paths with respective lengths $4n+1$ or $4n-1$). Then this theorem gives the (i,j)th element of $\mathbb{A}^{-1}$ as this effective number of conjugated paths between i and j. It is emphasized that in the case of trees, there is just one path between two vertices, so that the elements of $\mathbb{A}^{-1}$ take but one of the three values 0, -1, or $+1$. Moreover, it turns out that these signs may be »eliminated« under suitable conditions characterized in terms of an auxilliary graph: for G with a Kekule structure κ (viewed as a spanning subgraph with every vertex of degree 1), define the κ-contracted graph G_{con} to have vertex set $V(G_{\mathrm{con}}) = E(\kappa)$ and edges of G_{con} between $\{i,j\}$ and $\{k,l\} \in V(G_{\mathrm{con}})$ if there is an edge of G between a vertex of $\{i,j\}$ and a vertex of $\{k,l\}$. Also we recall that for an adjacency matrix $\mathbb{A}(G)$, with a normalized eigenvector $\mathbf{v}$ with components v_i, one says the associated eigenvector density (distribution) is $|v_i|^2$, $i \in V(G)$. The »sign-eliminatability« result then is:

Theorem H. – Let G be minimally Kekulenoid with G_{con} bipartite. Then the matrix $\mathbb{X}$ with elements the absolute values of those of $\mathbb{A}^{-1}$ has the same eigen-spectrum as $\mathbb{A}^{-1}$. Moreover there is a correspondence between the eigenvector densities for $\mathbb{X}$ and $\mathbb{A}$.

Proof: Each pair of neighbor sites of G connected by an edge in the unique Kekule structure κ of G is contracted to a single site of a contracted graph $G_{\mathrm{con},}$ which by hypothesis is bipartite. Thence the sites of G may be partitioned into two sets $V_+(G)$ and $V_-(G)$ corresponding to the »starred« and »unstarred« sites of G_{con}; that is,

$$i,j \in V_+(G) \Leftrightarrow \{i,j\} \in V_\star(G_{\mathrm{con}}) \quad \text{and}$$

$$i,j \in V_-(G) \Leftrightarrow \{i,j\} \in V_{\mathrm{o}}(G_{\mathrm{con}})$$

Then a diagonal matrix $\mathbb{U}$ may be introduced with elements $U_{ii} = \pm 1$ as $i \in V_{\pm}(G)$. Since $\mathbb{U}$ is unitary (with $\mathbb{U}^{-1} = \mathbb{U}^{\dagger} = \mathbb{U}$), it preserves the eigen-spectrum of $\mathbb{A}^{-1}$ under a similarity transformation (here $\mathbb{U}\mathbb{A}^{-1}\mathbb{U}^{-1}$). But it is readily seen that $\mathbb{U}\mathbb{A}^{-1}\mathbb{U}^{-1} = \mathbb{X}$, so that if $\mathbf{v}$ is an eigenvector of $\mathbb{A}^{-1}$, then $\mathbb{U}\mathbf{v}$ is an eigenvector of $\mathbb{X}$ with the same eigenvalue. Thus $\mathbb{A}^{-1}$ and $\mathbb{X}$ have the same eigenspectrum, and corresponding eigenvector densities. Moreover since $\mathbb{A}^{-1}$ and $\mathbb{A}$ have the same eigenvectors, it follows that $\mathbb{X}$ and $\mathbb{A}$ have corresponding eigenvector densities, and the theorem is proved.

Moreover one may specialize this result to an important case with the observation that if G is a Kekulenoid tree, then G_{con} is also a tree, and therefore bipartite. Thence one has:

Corollary I. – Let G be a Kekulenoid tree. Then the matrix $\mathbb{X}$ with elements the absolute values of those of $\mathbb{A}^{-1}$ has the same eigen-spectrum as $\mathbb{A}^{-1}$. Moreover the eigenvector densities for $\mathbb{X}$ and $\mathbb{A}$ correspond.

This result for the eignevalues has also been proved by Cvetković *et al.*[11] and by Godsil[12] (with the demonstration that $\mathbb{X}$ and $\mathbb{A}^{-1}$ have the same characteristic polynomials.) It may be further noted that the eigenvector densities are not graph invariants unless the associated eigenvalue is non-degenerate. However regardless of degeneracy correspondences of eigenvector densities still apply – in fact the phase matrix $\mathbb{U}$ in the proof of theorem H allows a correspondence of eigenvectors. Yet further Mukherjee and co-workers[16,17] have studied such graphs, giving several examples, and futher using their results in the evaluation of eigenspectra of more general graphs.

DIGRESSION ON KEKULENOID TRANSFORMS

Since the matrices $\mathbb{A}^{-1}$ of the preceding section, and even more more especially the $\mathbb{X}$, resemble adjacency matrices for graphs G^K, it is natural to define each such graph as the Kekulenoid transform of a minimally Kekulenoid graph G. Some examples of such transforms G^K for the case of G being a tree are given in Figure 3, where there is a suppression of the signs as arise without the imposition of theorem H (which allows their elimination). Cvetković *et al.*[11] define a »pseudo-inverse« of G which is[18] closely related to G^K (and often is the same as G^K). Mukherjee and co-workers[16,17] define »reciprocal« graphs simply as those with eigenvalues in inverse pairs, and illustrate several classes (each a homologous seqence) of such (also unweighted) graphs, which then turn out to be graphs for which $G = G^K$. Thence the current transform G^K may be surmised to be of some fundamental interest, and some points may be noted (several of which are noted by Cvetković *et al.* [11] in the circumstances that their »pseudo-inverse« coincides with G^K):

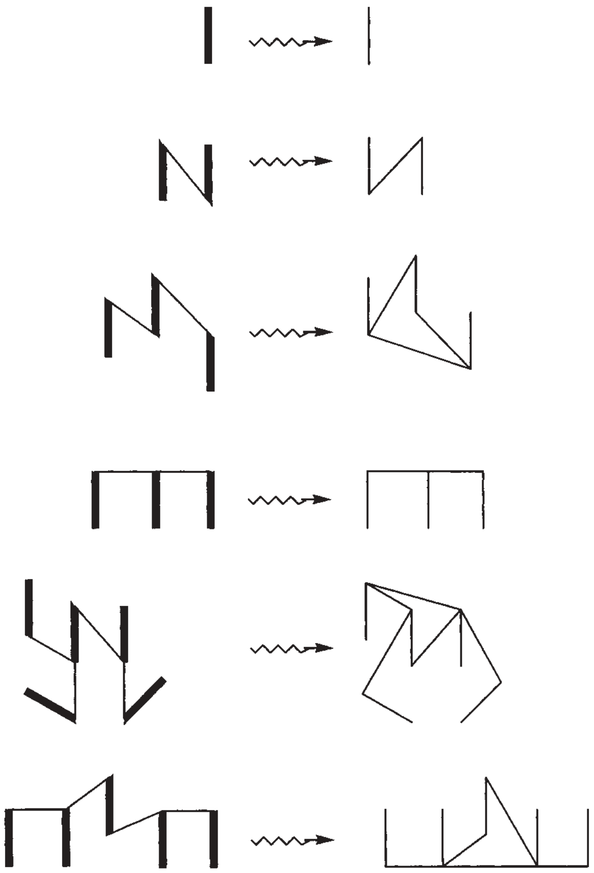

Figure 3. Kekulenoid transforms for some acyclic (minimally Kekulenoid) polyenes, with G and G^K separated by the transformation symbol of a »squiggly arrow«. The drawings do not simulate chemically preferred conformations for G, but rather configurations are chosen such that upon making the transformation to G^K while fixing the positions of the sites the result avoids crossing bonds.

Proposition J. – For a minimally Kekulenoid graph G,

- the numbers of vertices of G and G^K are the same;
- the numbers of terminal vertices of G and G^K are the same; and
- both G and G^K are Kekulenoid.

Proof: First, the property that G and G^K have the same number of vertices is evident, since $\mathbb{A}^{-1}$ and $\mathbb{X}$ are of the same size as $\mathbb{A}$. Second, whenever G has a terminal vertex i, there is a unique adjacent vertex i' which is a terminal vertex in but a single conjugated path (i',i), so that (by lemma F) the sole non-zero matrix element involving i' in G^K is that connecting it to i, and i' is a terminal vertex in G^K. Third, the same pairs of sites paired in the unique Kekule structure of G are seen also to be pairable as a Kekule structure in G^K. Fourth, the reciprocity of the eigenvalues for G and G^K is a direct consequence of the definition of G^K in terms of the inverse of the adjacency matrix of G.

Overall proposition J indicates that there is a degree of similarity between G and G^K, with there sometimes being a further degree of likeness:

Proposition K. – If a minimally Kekulenoid graph G is bipartite, then G^K is also, and the sets of vertices of different types (★ and ○) in G and G^K match.

Proof: Granted that G is bipartite, every conjugated path of G is between sites of opposite types (★ and ○), so that (again *via* lemma F) the bipartitioning of vertices for the two graphs must be the same.

Because of the now established degree of similarity of G and G^K, it is perhaps not surprising that sometimes G and G^K are isomorphic, as occurs in some cases in Figure 3. Some further examples for minimally Kekulenoid cycle-containing bipartite G are given in Figure 4.

Further because G^K is developed to be the graph with adjacency matrix the inverse of that of G, we have:

Proposition L. – For a minimally Kekulenoid G, the adjacency-matrix eigenvalues of G and G^K are reciprocals of one another. The eigen-spectra of G and $(G^K)^K$ are the same.

In the case that G and G^K are isomorphic (denoted ≈, including the transformation of »sign-elimination), the parent G is seen to have adjacency-matrix eigenvalues with an interesting property:

Corollary M. – For a minimally Kekulenoid tree G with $G^K \approx G$, $\mathbb{A}$ is its own inverse (upon making a suitable permutative similarity transformation, permuting both rows and columns of $\mathbb{A}$ in the same way, and the simple diagonal similarity transformation of theorem G). Also the eigen-spectrum for G consists of pairs of eigenvalues which are reciprocals of one another.

Indeed one might describe this as a »multiplicative« pairing property, in reminiscence of Coulson and Rushbrooke's[19,20] »additive« pairing property (of eigenvalues occurring as + and – additive inverses, for bipartite graphs with no non-bonding MOs).

Even when G^K and G are different there often seems to be a vaguely suggestive degree of similarity, perhaps beyond that indicated in propositions J and K. See also the Figure 5, where the signs (for the edges) are suppressed when possible (*via* theorem H, though when they cannot be suppressed, they are then indicated with a – sign in the diagram). Often in the examples given, the Kekulenoid transform of a Kekulenoid transform gives the original graph back. Indeed this might be imagined to often occur since as noted in the second part of proposition L, G and $(G^K)^K$ are iso-spectral.

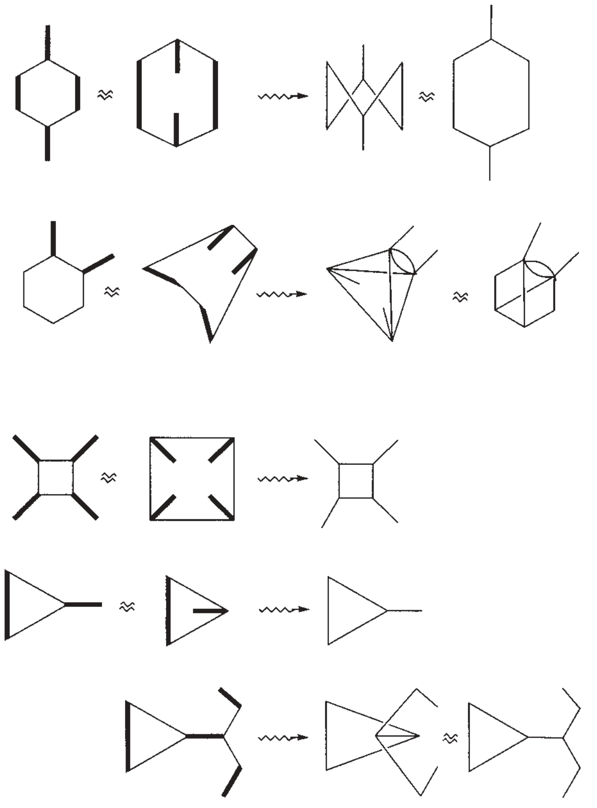

Figure 4. Kekulenoid transforms for some cycle-containing minimally Kekulenoid alternants. Alternative, more chemically pleasing configurations (or embeddings) to represent either the parent graph G or the transform G^K sometimes are also indicated (whence the different embeddings of the same graph are separated from one another by an equivalence sign ≈).

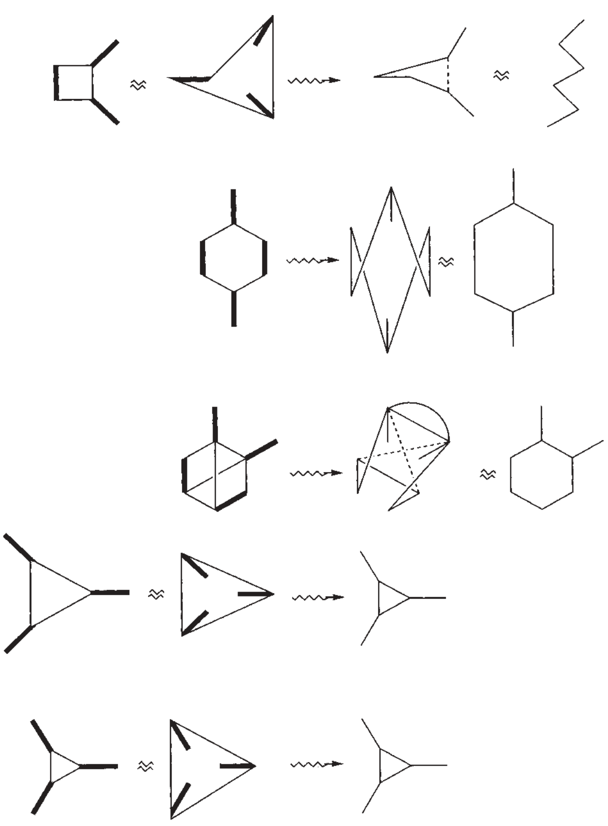

Figure 5. Kekulenoid transforms for additional minimally Kekulenoid species, entailing some (non-unit) weights when relevant. When there are both a + and – edges between the same pair of vertices, they cancel, but the result is indicated by a dotted edge.

BOUNDS FOR THE HOMO-LUMO GAP OF TREES

Notably the results (but not the proofs) of this section may be readily understood without attending to the bulk of the preceding results. Some standard graph-theoretic nomenclature (defined in earlier sections) is needed – including the less common definitions of »minimally Kekulenoid« and »conjugated path«. In a minimally Kekulenoid graph G (which by definition has exactly one Kekule structure) a conjugated path is an odd-length path with its own Kekule structure which is a subgraph of the Kekule structure of G. For a graph with adjacency matrix $\mathbb{A}$ let $\Delta \equiv \Delta(\mathrm{G})$ denote the difference between the two eigenvalues closest to 0. For a neutral hydrocarbon with a bipartite graph this is just the gap between highest-occupied MO and lowest-unoccupied MO within the context of the Hückel model. Let $p_i(\mathrm{G}) = p_i$ be the total number of conjugated paths which initiate at vertex i of a Kekulenoid graph G. Then further define some invariants

$$P_1(\mathrm{G}) \equiv \sum_i p_i$$
$$P_2(\mathrm{G}) \equiv \sum_i p_i^2$$
$$P_3(\mathrm{G}) \equiv \sum_{\{i,j\}}^{\mathrm{cp}} p_i\, p_j$$

where the first two sums are over all vertices of G, and the third sum is over all pairs of vertices between which there is a conjugated path. These conjugated-path invariants clearly encode information about conjugation patterns and chemically might naturally be expected to correlate in some manner to stability and reactivity. This we seek to do by way of using these invariants to bound the HOMO-LUMO gap Δ:

Theorem N. – For an N-site minimally Kekulenoid tree,

$$2N/P_1 \geq 2P_2/P_3 \geq \Delta \leq (2P_2/N)^{1/2}$$

Proof: The proof is motivated by and makes use of corollary J and the standard Rayleigh-Ritz variational principle, which has been used elsewhere[21] to set up a set of often good lower bounds to the maximum eigenvalue $\lambda_{\max}$ of a matrix such as $\mathbb{X}$. In the current context with the choice of an underlying (column) vector ϕ with all components =1, these previous results give lower bounds to $\lambda_{\max}$

$$(\phi^\dagger \mathbb{X} \phi) \,/\, (\phi^\dagger \phi) = P_1/N,$$
$$(\phi^\dagger \mathbb{X}^3 \phi) \,/\, (\phi^\dagger \mathbb{X}^2 \phi) = P_3/P_2, \text{ and}$$
$$\{(\phi^\dagger \mathbb{X}^2 \phi) \,/\, (\phi^\dagger \phi)\}^{1/2} = \{P_2/N\}^{1/2}$$

where $\mathbf{u}^\dagger$ denotes the (complex conjugate) transpose of $\mathbf{u}$. Since the eigenvalues of $\mathbb{X}$ and $\mathbb{A}$ are inverses, these bounds then lead to the first three upper bounds of the present theorem for $\Delta = 2/\lambda_{\max}$.

Additional higher order invariants turn out to be definable, and useable in higher order bounds to the HOMO-LUMO gap. To this end define $\mathbf{p}^{(0)} \equiv \phi$ as the N-vector with all components =1, and then recursively define $\mathbf{p}^{(n+1)}$ as the vector with components

$$p^{(n+1)}{}_i \equiv \sum_j^{\mathrm{cp}:i\to j} p^{(n)}{}_j$$

where the sum is over all conjugated paths from site i to any other site j. Then

Proposition O. – Let G be an N-site acyclic Kekulenoid graph with $\mathbf{p}^{(m)}$ as above. Then

$$\textstyle\sum_i p^{(m)}{}_i\, p^{(n)}{}_i$$

depends only on the sum m+n, and gives the graph invariant $P_{m+n.}$

Proof: In the notation of theorem H, the sum of this theorem is clearly

$$\mathbf{p}^{(m)\dagger}\mathbf{p}^{(n)} = \phi^\dagger \mathbb{X}^{\dagger m} \mathbb{X}^n \phi = \phi^\dagger \mathbb{X}^{m+n} \phi = P_{m+n}.$$

Thence a sequence of conjugated-path invariants P_m results, with P_1, P_2, and P_3 as already considered in the preceding paragraph. Now the whole sequence leads to further HOMO-LUMO gap estimators:

Theorem P. – Let G and P_m be as in proposition O. Define three sequences

$$\mathsf{S}_{\mathrm{even}} : \; 2(P_0/P_2)^{1/2},\, 2(P_2/P_4)^{1/2},\, 2(P_4/P_6)^{1/2},\ldots$$
$$\mathsf{S}_{\mathrm{odd}} : \; 2(P_1/P_3)^{1/2},\, 2(P_3/P_5)^{1/2},\, 2(P_5/P_7)^{1/2},\ldots$$
$$\mathsf{S}_2 : \; 2/\lambda_1,\, 2/\lambda_2,\, 2/\lambda_3,\, 2/\lambda_4,\ldots$$

with $\lambda_m \equiv \{B + (B^2 + AC)^{1/2}\}/A$, where $A = (P_{2\mathrm{m}}P_{2m+2} - P_{2m+1}{}^2)$, $B \equiv (P_{2m+3}P_{2m} - P_{2m+2}P_{2m+1})/2$, and $C \equiv (P_{2m+2}{}^2 - P_{2m+3}P_{2m+1})$. Then each sequence separately converges to the HOMO-LUMO gap $\Delta(\mathrm{G})$. Further the convergence for $\mathsf{S}_{\mathrm{even}}$ and S_2 is monotonic from the upper bound side.

Proof: Much as in theorem N the proof is motivated by and makes use of theorem H and the standard Rayleigh-Ritz variational principle, which has been used elsewhere[21] to set up sequences converging to the maximum eigenvalue $\lambda_{\max}$ of an adjacency matrix such as $\mathbb{X}$. Much as in theorem N the sequences of lower bounds converging to $\lambda_{\max}$ give sequences of upper bounds converging to $\Delta = 2/\lambda_{\max,}$ this time using theorems G and H of Ref. 21.

Theorem Q. – Let G and P_m be as in proposition O, and $p^{(m)}{}_{\mathrm{i}}$ be as just preceding proposition O. Then the quantity $(p^{(m)}{}_i)^2/(P_{2m})^{1/2}$ approaches the common density of the HOMO and LUMO orbitals on site i.

Proof: The vector $\mathbf{p}^{(m)}$ is identified as a power-method approximant to a linear combination of the maximum and minimum eigenvalues of $\mathbb{X}$. Generally the combination arises even in the large-m limit because they are of equal magnitude, as a consequence of the bipartiteness of the graph G^K corresponding to $\mathbb{X}$. But as a further consequence of the Coulson-Rusbrooke pairing theorem[17,18] these two eigenvalues have eigenvectors with the same density. See also corollary J. The density for $\mathbf{p}^{(m)}$ at site i is ~ $(p^{(m)}{}_i)^2$, which if normalized entails division by the factor $(\mathbf{p}^{(m)\dagger}\mathbf{p}^{(m)})^{1/2}$, which by proposition O is just $(P_{2m})^{1/2}$.

The type of bounds indicated in theorems N and P have been found[21] to be quite accurate, and the sequences rapidly converging, in a slightly different context. If desired, the (relative) amplitudes of the actual HOMO and LUMO eigenvector could be traced out *via* the phase transformation $\mathbb{U}$ in the proof of theorem H. The examples of the next section may be understood solely in terms of the results of N, O, P, and Q.

As an aside, it may be noted that a slightly more involved methodology ends up with results much like that of theorems N and P carrying over to an enlarged range of minimal Kekulenoids, beyond acyclics. In particular a minimally Kekulenoid graph G sometimes has an inverse $\mathbb{A}^{-1}$ from which signs may be simply deleted by a diagonal unitary similarity transformation, as described in the proof of theorem H. Then G may be termed sign-eliminatable, and one has:

Proposition R. – Let G be a sign-eliminatable minimally Kekulenoid graph. Then the bounds of theorem N hold as also do the bounded convergences of theorem P.

Argument: The proof is precisely as in the previous theorems, but the earlier theorems have been stated separately, since there is in them an especially ready criterion to recognize whether G is sign-eliminatable – namely the sufficient (but not necessary) condition that G is a tree.

Sufficient conditions for sign-eliminatability are given in theorem H. Notably this condition is not necessary, as witnessed by dimethenyl-cyclobutadiene, appearing in Figure 4.

EXAMPLES

The accuracy of the bounds might be tested in application to particular cases, such as in the sequence of (minimally Kekulenoid) acyclic polyenes whose first few members are indicated in Figure 6. The nth of these Kekulenoid trees with $N = 2n$ π-centers is denoted by T_n, and the local conjugated-path counts p_i $(= p^{(1)}{}_i)$ are as indicated also in the figure. These trees are of the special class of »self-inverse« structures (for which the eigen-spectrum is multiplicatively paired, such that for every eigenvalue λ there is a corresponding one $1/\lambda$). A pictorial manner of generation of the higher-order counts $p^{(n)}{}_i$ for the example of T_3 is indicated in Figure 7, and this leads to different order conjugated-path invariants,

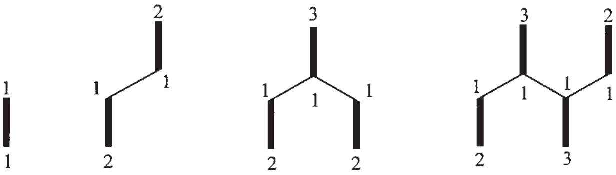

Figure 6. The first four members T_1, T_2, T_3, T_4 of an exemplar sequence of Kekulenoid trees.

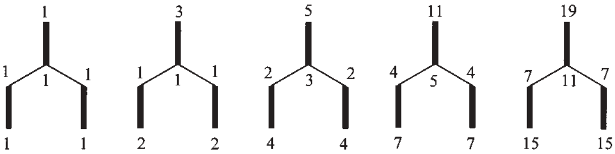

Figure 7. The recursive generation of the $p^{(m)}{}_i$, $m=0, 1, 2, 3$ for T_3.

$$P_0 = 6,\ P_1 = 10,\ P_2 = 20,\ P_3 = 38,\ P_4 = 74,$$
$$P_5 = 142,\ P_6 = 276,...$$

As a consequence one obtains sequences of bounds to Δ for T_3 :

S_{even} : 1.095445, 1.03975, 1.03559,...

S_{odd} : 1.02598, 1.03523, 1.03523,...

S_2 : 1.03654, 1.03541, 1.03529,...

Evidently each of these sequences approaches quite rapidly the exact HOMO-LUMO gap of $\Delta = \sqrt{6} - \sqrt{2} \approx 1.03527$.

As an aside it may be illustrated that the present approach can also be used to obtain exact results, *e.g.*, for butadiene (T_2), as indicated in Figure 8, where in addition to the first few recursions for the $\mathbf{p}^{(m)}$, the general recursion pattern is also indicated, from a mth-stage situation with local counts A and B at terminal and interior sites to the next stage where the corresponding local counts could be denoted A′ and B′. Then it is seen that

$$\begin{pmatrix} A' \\ B' \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix}$$

or if expressed in terms of our unabbreviated notation

$$\begin{pmatrix} p^{(m+1)}{}_{\text{end}} \\ p^{(m+1)}{}_{\text{int}} \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} p^{(m)}{}_{\text{end}} \\ p^{(m)}{}_{\text{int}} \end{pmatrix}$$

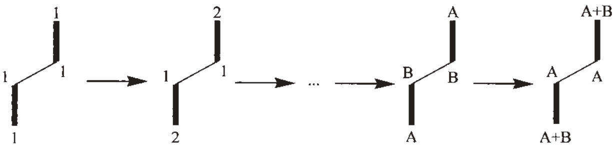

Figure 8. The general pattern of recursive generation of the $p^{(m)}{}_i$ for T_2.

where the subscripts identify end and interior sites of T_2. As a consequence the little 2 × 2 »transfer matrix« appearing here governs the behavior of the $p^{(m)}_{i.}$ The recursion is conveniently solved upon considering the form the recursion takes if the transfer matrix is diagonalized, and one is lead to

$$p^{(m)}_{\text{end}} = C_+\cdot\xi_+{}^{m} + C_-\cdot\xi_-{}^{m} \quad \text{and}$$

$$p^{(m)}_{\text{int}} = C_+\cdot\xi_+{}^{m-1} + C_-\cdot\xi_-{}^{m-1}$$

with $\xi_\pm \equiv (1 \pm \sqrt{5})/2$ the eigenvalues of the transfer matrix. Asymptotically (for $m\to\infty$) the maximum eigenvalue (ξ_+) dominates. But in this limit the approximants for Δ become exact (as noted in theorem P), and the $\mathbf{p}^{(m)}$ approach (up to normalization) a vector giving the density of the HOMO and LUMO (as noted in theorem Q). That is, $\Delta = (1+\sqrt{5})$ and the respective densities at the end and interior sites are $\xi_+\mathfrak{N}$ and $\mathfrak{N}$, with $\mathfrak{N}$ a suitable normalization.

The HOMO-LUMO site density may be obtained either as an estimate from the numerical progression of the $\mathbf{p}^{(m)}$ (used in generating the P_m) or as an exact limiting ($m\to\infty$) result from the recursive analysis, and the result has implications. Notably this density is larger for the terminal sites of butadiene, as is consistent with these sites' higher reactivity, say to the addition of bromine, which adds selectively to the terminal sites (as noted over a century ago by Thiele[22] in developing his theory of partial valence and bond delocalization).

Though this technique to make exact solutions generally becomes more involved (with larger transfer matrices for larger graphs G), it turns out rather simply to apply in the long-polymer limit for $T_{n.}$ Within the bulk »interior« of such a high-polymer chain T_n one anticipates that there are just two counts $p^{(m)}_i$ at the two types (degree 1 and 3) of translationally inequivalent sites in a monomer unit. If at a given stage m these two counts might be denoted by A and B, as indicated in the first part of Figure 9, then the counts (A′ and B′) at the next stage m+1 can be determined. Notably a conjugated path starting adjacent to a degree-1 site is at the end of just a single such path: that of length 1 to the adjacent degree-1 site. But starting from an interior degree-1 site one sees that there are just three conjugated paths: one of length 1 to the adjacent degree-3 site, and two of length 3 to the degree-1 sites in the adjacent monomer units. Thence, as indicated also in Figure 9,

$$\text{A}' = \text{B} + 2\text{A} \quad \text{and} \quad \text{B}' = \text{A}$$

or if expressed in terms of our unabbreviated notation

$$\begin{pmatrix} p^{(m+1)}{}_a \\ p^{(m+1)}{}_b \end{pmatrix} = \begin{pmatrix} 2 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} p^{(m)}{}_a \\ p^{(m)}{}_b \end{pmatrix}$$

Again a 2 × 2 transfer matrix arises, and leads to solutions

$$p^{(m)}{}_a = \text{C}_+\cdot\xi_+{}^{m} + \text{C}_-\cdot\xi_-{}^{m} \quad \text{and}$$

$$p^{(m)}{}_b = \text{C}_+\cdot\xi_+{}^{m-1} + \text{C}_-\cdot\xi_-{}^{m-1}$$

where now $\xi_\pm \equiv 1 \pm \sqrt{2}$ are the eigenvalues of the current transfer matrix. Of course the maximum root here dominates in the large-m limit, whence one also has

$$P_m \approx nA_+(1 + \xi_+)\, \xi_+{}^{m-1}$$

and the HOMO-LUMO gap is

$$\Delta \cong 2/\xi_+ = 2(\sqrt{2} - 1)$$

which is exact in the limits that $n\to\infty$ and $m\to\infty$. Again the relative values of the $p^{(m)}_i$ allow a prediction of relative reactivities, with the degree-1 sites (also again) being predicted to be more reactive (in the sense of having higher HOMO-LUMO densities).

The oligomers T_n are rather special, and the whole eigen-spectrum may be analytically obtained *via* conventional eigenvalue techniques (as noted in Ref. 23, though these authors have an error in their formulas). The corrected adjacency-matrix eigenvalues are

$$\varepsilon_{j\pm} = \cos[j\pi/(n+1)] \pm \{1 + \cos^2[j\pi/(n+1)]\}^{1/2}, \qquad j = 1\to n$$

along with the negatives of these values. Thence of course the HOMO-LUMO gaps are also obtainable analytically. Still this sequence provides a nice test of the current estimators for Δ. Some part of the conjugated-path counts may also be carried out in general. For general T_n one may verify that

$$P_0 = 2n,\ P_1 = 4n - 2,\ P_2 = 10n - 10,$$
$$P_3 = 24n - 34,\ P_4 = 58n - 82,\ \text{P}_5 = 140\text{n} - 294$$

and utilize these in various estimates for Δ. The behavior of the even sequence S_{even} is indicated in Figure 10 for a few different T_n. Anticipating exponentially fast convergence, we have plotted logarithms of errors for the approximants from the even sequence of theorem P. In fact the convergence does seem to be exponentially fast, and similar tests with the two other sequences of approximants leads to similarly rapid convergence.

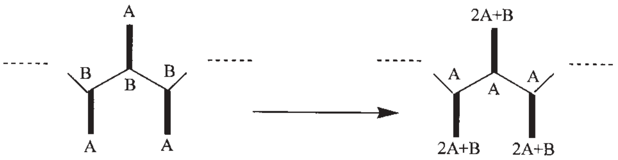

Figure 9. The general pattern of recursive generation of the $p^{(m)}_i$ in the (deep) interior of a very long chain T_n.

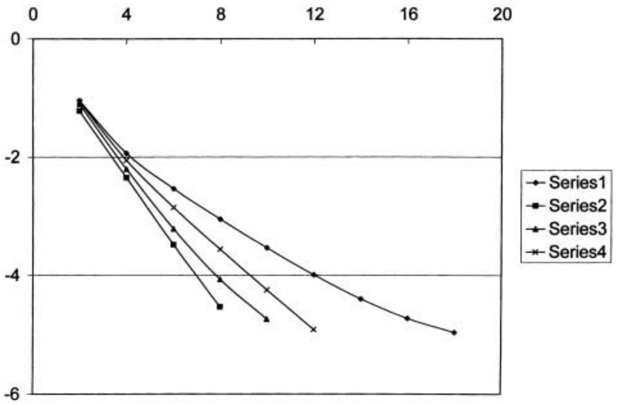

Figure 10. A plot of the logarithms (base-10) of the deviations of the approximants $\Delta_{\text{even}}^{(m)}$ from the exact gap Δ as a function of the order *m* of approximation, for a few different trees, T_3, T_4, T_5, and T_6 in proceeding from the left to the right.

CONCLUDING REMARKS

Here we have introduced or refined several novel graph-theoretic concepts, proved a suite of related theorems, and established some graph-theoretic (upper-bounding) estimates for HOMO-LUMO gaps of minimally Kekulenoid conjugated networks. Special focus has been directed to acyclic (Kekulean) polyenes, such as incidentally might be mentioned have recently been[24] extensively enumerated (and otherwise graph-theoretically characterized), the number of structural isomers much exceeding a million by $N = 30$ sites. Some illustrative example applications of the present results for the HOMO-LUMO gap have been made.

But it is emphasized that beyond quantitative formulas, our present results, especially as indicated in our example section, indicate some general qualitative chemical conclusions, for minimally Kekulenoid acyclic polyenes:

(1) In the comparison of different such species, the HOMO-LUMO gap Δ is smaller if there is a larger profusion of conjugated paths. [The longer the conjugated paths, the smaller the gap.]

(2) In the comparison of reactivities of different sites within a given such species, sites from which there initiate greater numbers of conjugated paths are more reactive. [In particular, terminal (degree-1) sites are more reactive than the adjacent sites.]

The first of these general conclusions is seen from the formulas (of theorems N and P) for the Δ approximants (involving the conjugated-path invariants), and further this general conclusion might be chemically rationalized: for if there are few conjugated paths, then a system might be anticipated to act like a small polyene (*e.g.*, ethylene or butadiene) also with few conjugated paths, and so like the small molecules manifest larger gaps Δ. Further the theorems give a quantitative meaning to »profusion« in this first general conclusion. The second general conclusion is seen in the manner in which the higher-order conjugated-path counts $p^{(m)}{}_i$ develop (to give the HOMO and LUMO densities as indicated in theorem P), and this result might be rationalized by arguing that a site from which many conjugated paths initiate has longer-range contributions to its bonding such as can then be more readily broken to form addition compounds. Moreover, as we have already noted this second general conclusion is in agreement with some (limited) experimental observations.

Of particular chemical interest is that our results evidently relate to what in a fair body of experimental chemical literature is often called cross conjugation. See, *e.g.* Refs. 25, 26, 27, 28, 29. Cross conjugation occurs when one double bond, say β, is conjugated to two others, say α and γ, while α and γ do not lie in a common conjugated path. As a consequence cross conjugation delimits the length of conjugation paths, so that the two chemical conclusions above for acyclic (Kekulenoid) polyenes might be restated as:

(1′) In the comparison of different such species, the HOMO-LUMO gap Δ increases with cross conjugation.

(2′) In the comparison of reactivities of different sites within a given such species, sites at which cross conjugation occurs are less reactive. [In particular, terminal (degree-1) sites are more reactive than the adjacent sites.]

The earlier largely experimentally oriented chemical considerations seem primarily focused on cross conjugation as an alternative structural feature besides linear and cyclic conjugation, and much of the focus seems to be on (often non-alternant) cycle-containing species with cross conjugation and sometimes with hetero-atoms. Thus though this chemical interest is broader than the focus attained here, the quantitativeness of the present resultant consequences may be of much interest in this area.

But further much of our current general conclusions perhaps often extend beyond acyclics to general minimally Kekulenoid alternants (though our intermediate theorems reveal that there can sometimes arise cancellations between different conjugated paths, of suitable different lengths, so as to reduce effective conjugated-path counts). The idea that conjugated paths and particularly their counts relate to stability and reactivity seems chemically natural as these encode some information about conjugation patterns, which should have some manifestation beyond that of conjugated circuits and their counts, as also proposed in 1987 by Randić and Trinajstić.[6] Indeed they further emphasize the likely crucial character of conjugated paths when there are no conjugated circuits. Thus the present use of conjugated paths to characterize HOMO-LUMO gaps and local reactivities of minimally Kekulenoid species provides a quantitative realization of Randić and Trinajstić's idea that such paths should be chemically relevant. Presumably even beyond the case of minimally Kekulenoid hydrocarbons, conjugated paths should turn out to be of chemical relevancy.

In the present development of the HOMO-LUMO gap estimates, some novel mathematical ideas have been described and inter-related, including: adjacency-matrix inversion, conjugated paths, and »Kekulenoid transforms«, at least in the context of minimally Kekulenoid graphs. Perhaps other chemical graph theoreticians such as Nenad Trinajstić or Milan Randić may find intriguing possibilities with the approaches here taken to these ideas.

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SAŽETAK

Minimalno-kekulenoidne π-mreže i reaktivnost acikličkih konjugiranih poliena

Douglas J. Klein i Anirban Misra

Grafove koji dopuštaju samo jednu Kekuléovu strukturu autori su nazvali minimalno-kekulenoidni grafovi. Autori smatraju da oni predstavljaju zanimljivu klasu konjugiranih π-mreža, koje su istražili, naročito za slučaj alternantnih struktura. Konstruirane su inverzne matrice susjedstva takovih molekularnih grafova i nađeno je da predstavljaju (opće bridno-utežane) matrice susjedstva kekulenoidno-transformiranoga grafa. Te su transformacije istražene. Opaženo je da su stabla ili nekekulenoidna ili minimalno-kekulenoidna. Pokazano je da je kekulenoidna transformacija naročito jednostavna za minimalno-kekulenoidne slučajeve. Također su izvedene granice za HOMO-LUMO razmak za acikličke konjugirane poliene pomoću konjugiranih staza. Nekoliko je primjera prikazano, a identificirane su i neke kemijske posljedice unakrižne konjugacije.