EIGENVALUES OF SATURATED HYDROCARBONS

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ABSTRACT. A simplified Hückel-type molecular-orbital (MO) model for the valence electrons of saturated hydrocarbons is proposed and the consequent eigenvalue spectrum considered. A first foundational result is obtained, which every chemist "knows", namely that: alkanes are stable, with half their (Hückel-type MO) eigenvalues positive and half negative.

Keywords: saturated hydrocarbons, alkanes, stellation, para-line graph.

1. SATURATED HYDROCARBONS AND THE STELLATION MODEL

Saturated hydrocarbons have long (that is, for well more than a century) served as the foundational introduction to organic chemistry. During the last four decades chemical graph theory has become prominent—much of it dedicated to classical Hückel theory of conjugated π-electron networks, where the Hückel Hamiltonian coincides (up to a shift and scale) with the mathematical graph-theoretic adjacency matrix, for example, as emphasized in [12]. Along with this application of mathematical graph theory there has been extensive development of an extensive array of molecular topological indices, mostly for uses in QSAR, for example, as reviewed in [5]. Yet there has also been a sporadic array of several other usages of chemical graph theory, say as in isomer enumeration, for example, with a special issue of MATCH devoted to this [7]. But what is (possibly) amazing is that there has been practically no effort to use chemical graph theory for describing the electronic structure of molecules other than conjugated hydrocarbons.

Here a step is taken towards the rectification of this utter paucity of application of mathematical graph theory to other comparable electronic-structure problems. In particular, here a simple Hückel-type MO model for the valence electrons of saturated hydrocarbons is described and then some first consequential results are obtained.

Definition 1.1. A *saturated hydrocarbon* is a connected graph whose vertices have both degrees one and four and no other degrees.
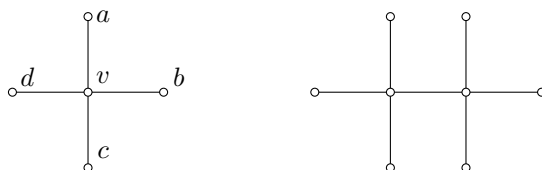
FIGURE 1. The graphs of the saturated hydrocarbons methane CH_4 and ethane C_2H_6. These are both alkanes. The degree-one vertices correspond to H atoms and the degree-four sites correspond to C atoms.

The degree-4 and degree-1 vertices respectively correspond to C and H atoms. See, for example, Figure 1. The present electronic-structure model is framed in terms of the four sp^3-hybrid orbitals of each carbon atom along with the single 1s-orbital of each hydrogen. The *stellated graph* G^* associated to this model for a saturated hydrocarbon has a *vertex* set $V^* = V(G^*)$ corresponding to each of these orbitals (four for each C and one for each H) with an *edge* set $E^* = E(G^*)$ partitioned into two subsets of edges, namely *internal* edges E^*_{int} and *external* edges E^*_{ext}. This internal set consists of six edges for the four hybrid orbitals of each C atom (that is, each such orbital in a C atom is bonded or linked together by an edge of E^*_{int}), and each external bond $e^* \in E^*_{ext}$ corresponds to a unique edge e of G interconnecting the same pair of atoms—each vertex of G^* is connected to a unique other vertex (of G^*) in the other atom to which e connects. Thus, for example, methane and ethane commonly denoted in Figure 1 give rise to the electronic structure graphs G^* of Figure 2, where the external edges are shown in bold. Chemically, each C-atom hybrid (represented by a $v^* \in V^*$) points along one bond direction to interact with a unique other orbital in another atom (such as indicated in G), while also there are interactions amongst the hybrids within the same atom.

Mathematically one may represent the vertex and edge sets of G^* thusly.

Definition 1.2. The *stellation* of a graph G is the graph G^* with vertices $V(G^*) = \cup_{ab \in E(G)} \{(a,b), (b,a)\}$. Vertices $(x,y), (z,w) \in V(G^*)$ are adjacent if, and only if, either $x = z$ or both $x = w$ and $y = z$. Then $E^*_{int} = \{(a,b)(b,a) : a \sim b \text{ in } G\}$, $E^*_{ext} = \{(a,b)(a,c) : a \sim b \text{ and } a \sim c \text{ in } G\}$, and $E(G^*) = E^*_{int} \cup E^*_{ext}$.

Clearly , $|V(G^*)| = 2|E(G)|$, and $|E^*_{ext}| = |E(G)|$. Note that, for a fixed vertex v, the vertices in the set $\{(v,a) : v \sim a \in V(G)\}$ form a clique in G^*. Note too that the external edges form a perfect matching (or "Kekule structure") of G^*.

Now our stellated graphs are complicit in much early work on alkanes. For representative historic examples see Sandorfy [22], Fukui et al. [8], or Pople and Santry [19] (or in a much more disguised form in Hoffmann [14]). More recently there has been some modest amount of work also, for example, in [9, 10]. But in all these these works, the aim seems to be to develop an elaborate parameterization to closely mimic (SCF) ab initio computations so as to enable facile application to individual molecules, one after another, after another, etc. In contrast here, we propose simplified models for which general theorems might be developed for whole (infinite) classes of molecules. Recently on the mathematical side, *para-line graphs* have been described [23] as derived from a parent graph by taking the line graph of the graph obtained via subdivision of the edges of G. Indeed then this para-line graph is our stellated graph G^*.

In these earlier chemical works [22, 8, 19, 10, 9] the graph becomes quite decorated with different weights. Amongst such modifications, the most important gives different weights to the internal and external graph edges—appropriate weightings for the internal edges being in the neighborhood of half the weighting for the external edges (whose weights we take $= 1$). In this earlier work the C-C and C-H external bonds are weighted differently, typically differing in weight by $<10\%$, so it seems a not too unreasonable approximation for our general purposes to treat these as equivalent. A more severe approximation which we here also make is to treat the orbitals of the H and C atoms as equivalent (i.e., to take their diagonal matrix elements equal, here shifted to $= 0$)—in a better imitation of reality these should differ from one another by roughly $1/4$ of the C-C (external edge) interaction.

A common introductory chemistry description neglects the internal interactions to leave only the external interactions, with an externally bonded pairs forming C-C or C-H bond orbitals, each of which is then doubly occupied (spin-up and spin-down)—see also Pople and Santry [19, Theorem 1]. (That our theorem makes notably less severe presumptions on the parameter values, indicates its conceptual value, as Pople and Santry viewed such a weaker theorem important to state.) The other antisymmetric bond orbitals play a role in the excited states of saturated hydrocarbons [13, 20]. Finally some other possible early realizations of our stellated graphs are mentioned in our conclusions.

2. Results

For a stellated graph G^* with vertex set $V(G^*) = \{v_1, \ldots, v_n\}$ we define a weighted adjacency matrix A^w as follows: $A^w_{i,j} = 1$ if $v_i v_j$ is an external edge in G^*, $A^w_{i,j} = w$ if $v_i v_j$ is a internal edge, and $A^w_{i,j} = 0$ otherwise. A^w is the *weighted*
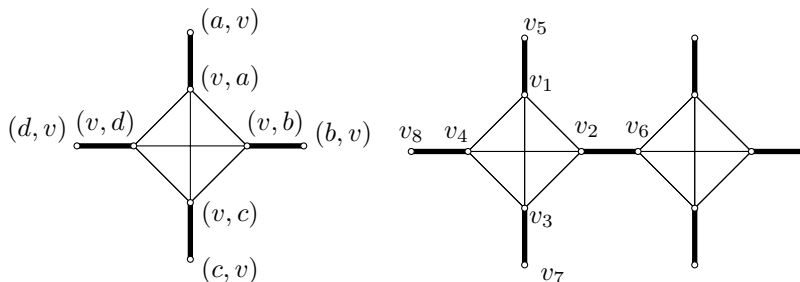
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FIGURE 2. The stellated graphs of the saturated hydrocarbons methane CH_4 and ethane C_2H_6. The pendant edges and edge v_2v_6 have unit weight. These are (the highlighted) external edges corresponding to the edges of CH_4 and C_2H_6. The internal edges, forming four-element cliques, are edges with weight w. For stellated methane and ethane with internal edges of *any* weight, the determinant is, respectively, 1 and -1. Lemma 2.2 then implies that half the eigenvalues are positive and half are negative. With internal weights $w = 0.5$, the eigenvalues are (approximately) 2.0, 0.78, 0.78, 0.78, -0.5, -1.28, -1.28, -1.28.

adjacency matrix for G^*, and typically $w \in [0, 1)$. When no confusion is possible, we abuse notation and denote the weighted adjacency matrix of G^* by "G^*".

We utilize the definition of the determinant of a matrix, defined as follows.

Definition 2.1. The *determinant* of an $n \times n$ square matrix A with entries $A_{i,j}$ is

$$\det A = \sum_{\sigma \in S_n} sgn(\sigma) \prod_{i=1}^{n} A_{i,\sigma(i)},$$

where S_n is the set of permutations from $[n]$ to itself and $sgn(\sigma)$ is 1 if σ can be written as an even number of permutations and -1 otherwise.

Lemma 2.2. *Let G be a graph with a perfect matching M, with edges in M having unit weight and remaining edges weighted w in a (non-trivial) interval $I \subseteq \mathbb{R}$ containing 0, and corresponding (weighted) adjacency matrix A^w. If $\det A^w \neq 0$ for all $w \in I$ then A^w has half positive and half negative eigenvalues for each $w \in I$.*

Proof. Let G be a graph with a perfect matching M, with edges in M weighted one and remaining edges weighted $w \in I$. Let A^w be the corresponding (weighted) adjacency matrix and $\det A^w \neq 0$.

Since M is a perfect matching, in the case where $w = 0$, A^w is a 0-1 matrix which is the same as the adjacency matrix for the graph induced on M. This graph

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has $|M|$ positive $(+1)$ and $|M|$ negative (-1) eigenvalues. The determinant $\det A^w$ is a continuous function of w and, as w varies, the eigenvalues vary continuously. No eigenvalue of A^w can equal 0 for any $w \in I$, for if it did then $\det A^w = 0$, contradicting our assumption. Since no eigenvalue can be 0, no eigenvalue can change sign—it would have to cross through 0—and the number of positive and negative eigenvalues remains constant for every $w \in I$. Since half are positive and half are negative when $w = 0$ it follows that half are positive and half are negative for every $w \in I$. $\qquad \square$

We now prove complete results for acyclic and unicyclic saturated hydrocarbons, followed by results in the general case.

Definition 2.3. An *alkane* is an acyclic saturated hydrocarbon.

Alkanes, by definition, are trees whose vertices have both degrees one and four and no other degrees. They include methane and ethane (see Figure 1).

Lemma 2.4. *Every alkane has a vertex adjacent to either* 3 *or* 4 *pendant vertices.*

Proof. Let G be an alkane. Let v and w be vertices at maximum distance in G. v and w are necessarily pendant vertices. Let $v = v_1, \dots, v_k = w$ be a shortest path between these vertices. v_{k-1} must have degree four. Let a and b be the non-path neighbors of v_{k-1}. a and b must both be pendants. Assume a is not a pendant. Let a' be any neighbor of a besides v_{k-1}. There is a unique path $v = v_1, \dots, v_{k-1}, a, a'$ from v to a'. This path has length $k+1$ contradicting the assumption that the path from v to w has maximum length. Thus, v_{k-1} has either just the three pendant neighbors a, b and w or, in the case that $k = 2$ and v is adjacent to v_{k-1}, four pendant neighbors a, b, v and w. $\qquad \square$

Theorem 2.5. *If G is an alkane then its stellation G^* has half positive and half negative eigenvalues for any real number internal edge weight w.*

Proof. The statement is true for the graph $K_{1,4}$ (corresponding to methane CH_4) representing the smallest alkane: the stellation of this graph has non-zero determinant, for any real number internal edge weight w. The claim then holds by Lemma 2.2. Assume then that the claim holds for any alkane with fewer than n vertices.

Let G be an alkane with n vertices. Lemma 2.4 implies that G has a vertex with three pendant neighbors a, b and c. Let G_v be the alkane formed by removing vertices a, b and c from G, together with incident edges. By assumption $\det G_v^* \neq 0$ for any internal edge weight w. We will show that $\det G^* = -\det G_v^*$ for any internal edge weight w and, thus, $\det G^* \neq 0$.

The vertices of G^* include $(v, a), (v, b), (v, c), (a, v), (b, v)$, and (c, v). Assume G^* has m vertices. Let $v_{m-5} = (v, a)$, $v_{m-4} = (v, b)$, $v_{m-3} = (v, c)$, $v_{m-2} = (a, v)$, $v_{m-1} = (b, v)$, and $v_m = (c, v)$. So v_{m-i} is adjacent to v_{m-i-3} for $i \in \{0, 1, 2\}$.

Now

$$\det G^* = \sum_{\sigma \in S_m} sgn(\sigma) \prod_{i=1}^{m} G^*_{i, \sigma(i)}.$$

Any non-zero summand in this expression corresponds to a permutation $\sigma \in S_m$ that sends the index of a pendant vertex to that of its neighbor, and the index of the neighbor back to the index of the pendant. It follows that σ contains the transpositions $(m - i, m - i - 3)$ for $i \in \{0, 1, 2\}$. Since these correspond to external edges their weights are 1; that is, $G^*_{m-i-3, \sigma(m-i-3)} = G^*_{m-i, \sigma(m-i)} = 1$ for $i \in \{0, 1, 2\}$. Then

$$\det G^*_v = \sum_{\sigma' \in S_{m-6}} sgn(\sigma') \prod_{i=1}^{m-6} G^*_{v_i, \sigma'(i)}.$$

Let $\sigma' \in S_{m-6}$ be any permutation corresponding to a non-zero summand in $\det G^*_v$. The non-zero summands in $\det G^*$ and $\det G^*_v$ are in bijective correspondence, where $\sigma \in S_m$ must have the form $\sigma = \sigma'(m - 5, m - 2)(m - 4, m - 1)(m - 3, m)$, with $sgn(\sigma) = -sgn(\sigma')$. Thus the non-zero summands of $\det G^*$ are exactly the negatives of the non-zero summands of $\det G_v$. So $\det G^* = -\det G^*_v$ for any internal edge weight w, and $\det G^* \neq 0$ by the inductive assumption. Lemma 2.2 then implies that G^* has half positive and half negative eigenvalues for any real number edge weight w. $\square$

Lemma 2.6. *If C_{2k} is an even cycle with edge weights alternating between 1 and $w \in (0, 1)$ then $\det C_{2k} \neq 0$.*

Proof. By definition,

$$\det C_{2k} = \sum_{\sigma \in S_{2k}} sgn(\sigma) \prod_{i=1}^{2k} C_{2k_{i, \sigma(i)}}.$$

There are three possibilities for the permutations corresponding to the non-zero summands. In the first case, for each of the edges weighted w, the permutation associates each edge endpoint to the opposite endpoint. In this case the summand will equal $(-1)^k w^{2k}$, as each of the k transpositions contributes w^2 to the product. In the second case, for each of the edges weighted 1, the permutation again associates each edge endpoint to the opposite endpoint. In this case the summand will equal $(-1)^k 1$, as the permutation can be represented as k transpositions and each of the $2k$ terms in the product equals 1. In the third case, the permutation is cyclic. If $V(C_{2k}) = \{v_1, \ldots, v_{2k}\}$, then there are two non-zero cyclic permutations:
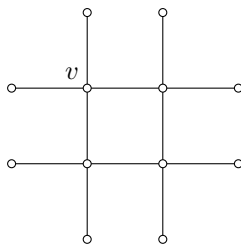
FIGURE 3. The graph G of the saturated hydrocarbon cyclobutane C_4H_8.

$(1, 2, \ldots, 2k)$ and $(2k, 2k - 1, \ldots, 1)$. In this case the permutation can be written as $2k - 1$ transpositions and each summand will equal $(-1)^{2k-1}w^k$.

Thus $\det C_{2k} = (-1)^k w^{2k} + 2(-1)^{2k-1}w^k + (-1)^k$. If k is even, then $\det C_{2k} = w^{2k} - 2w^k + 1 = (w^k - 1)^2$. If k is odd, then $\det C_{2k} = -w^{2k} + 2w^k - 1 = -(w^k - 1)^2$. In either case, for $w \in [0, 1)$, $\det C_{2k} \neq 0$. $\qquad\square$

Lemma 2.7. *If G is a saturated hydrocarbon formed from a cycle with two pendants attached to each vertex then the stellated graph G^* with unit weight external edges and internal edges with weight $w \in [0, 1)$ has half positive and half negative eigenvalues.*

Proof. Let G be a saturated hydrocarbon formed from a cycle C_k with two pendants attached to each vertex. Let G^* be the stellation of G. G^* will consist of a cycle of k order-four cliques with two pendants adjacent to each clique. See Figures 3 and 4 for an example. Note that the pendant vertices of G remain pendant vertices in G^*. The edges incident to these pendant vertices are external edges of G^* and have weight 1. Any non-zero summand of $\det G^*$ must correspond to a permutation that sends the index of any pendant vertex to the index of its unique neighbor and, reciprocally, the index of any neighbor of a pendant to the index of the pendant. The associated factors in the product are 1. Thus for a permutation σ corresponding to a non-zero summand of $\det G^*$ the only values which are not forced are those corresponding to a cycle C_{2k} which has edge weights alternating between 1 and $w \in [0, 1)$. That is, we have argued that $\det G^* = \det C_{2k}$. Lemma 2.6 implies that $\det C_{2k} \neq 0$ and, thus, $\det G^* \neq 0$. Lemma 2.2 then implies that G^* has half positive and half negative eigenvalues, which was to be shown. $\qquad\square$

Theorem 2.8. *If G is a unicyclic saturated hydrocarbon then its stellation G^* has half positive and half negative eigenvalues for any internal edge weight $w \in [0, 1)$.*

Proof. Lemma 2.7 implies that the statement is true for the smallest unicyclic saturated hydrocarbons. So we will assume that the statement is true for unicyclic
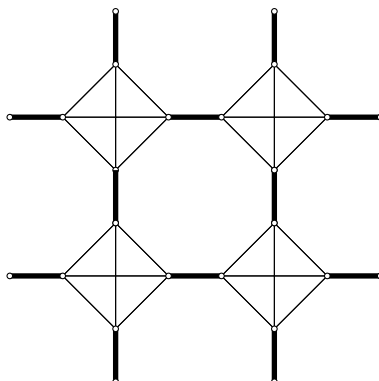
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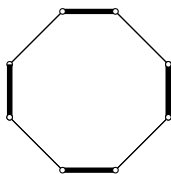FIGURE 4. The stellation G^* of cyclobutane C_4H_8.

FIGURE 5. What remains of the stellation G^* of cyclobutane C_4H_8 after the pendant edges and incident vertices are removed. The external edges are highlighted.

saturated hydrocarbons with fewer than n vertices and prove the truth of the statement for a unicyclic saturated hydrocarbon G with n vertices.

We can assume that G is not of the form of the graphs in Lemma 2.7, which consist of cycles with two pendants attached to every vertex. By definition G has a cycle; but there must be a vertex at distance greater than one from this cycle. Let C be the cycle and v be a vertex at maximum distance from C. (For a pair of vertices x, y, $d(x, y)$ is the *distance* from x to y, the length of the shortest path from x to y. For every vertex w we let $d(w, C) = \min\{d(u, w) : u \in V(C)\}$; then $d(v, C) = \max\{d(w, C) : w \notin V(C)\}$.) Now by imitating the argument of Lemma 2.4, we can assume that v' is adjacent to three pendants a, b and c. We then let G_v be the saturated hydrocarbon formed by deleting these pendants. G_v is unicyclic as we are deleting pendants away from the cycle C. Since G_v is a unicyclic saturated hydrocarbon with fewer than n vertices it follows that G_v^* has half positive and half negative eigenvalues and, hence, $\det G_v^* \neq 0$. And by imitating the argument of Theorem 2.5 we can show that $\det G^* = -\det G_v^*$ and, thus, that $\det G \neq 0$. Lemma 2.2 then implies that G^* has half positive and half negative eigenvalues.

$\square$

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Theorem 2.9. *Any stellated saturated hydrocarbon with external edges of unit weight and internal edges with weights $w \in [0, c)$ has half positive and half negative eigenvalues, for some molecule-dependent constant $c > 0$.*

Proof. The statement is true for the graph $K_{1,4}$ (corresponding to methane CH_4), representing the smallest saturated hydrocarbon: the stellation of this graph has half positive eigenvalues and half negative eigenvalues. The statement is true for acyclic and unicyclic saturated hydrocarbons. Theorems 2.5 and 2.8 show that any constant will work in the former case, while 1 works in the latter case.

Let G be any saturated hydrocarbon. Let G^* be its stellation with unit external edge weights and internal edge weights w. The statement is true in the case where $w = 0$: in this case the statement is equivalent to the fact that the eigenvalues of a union of K_2's (a graph consisting of disjoint edges) are half "+1" and half "−1". We now argue that there is a constant $c > 0$ so that, for any $w \in [0, 1)$, G^* has half positive and half negative eigenvalues.

Since we know that $\det G^*$ is a continuous function of w and that $\det G^* \neq 0$ when $w = 0$ there must be some (non-degenerate) interval $I \subseteq \mathbb{R}$ containing 0 for which $\det G^* \neq 0$ for every $w \in I$. Then let $c = \sup I$. The statement then follows. $\square$

We believe that the molecule-dependent constant c in Theorem 2.9 is in fact independent of the molecule and, following the case of unicyclic saturated hydrocarbons, is 1. Thus we conclude with the following conjecture. Further corroborative data is contained in the next section.

Conjecture 2.10. *Any stellated saturated hydrocarbon with external edges of unit weight and internal edges with weights $w \in [0, 1)$ has half positive and half negative eigenvalues.*

3. Data

B. McKays' *nauty* program [16] was used to generate all of the saturated hydrocarbons with up to 14 vertices. As a numerical experiment, the internal edges of the stellations of these graphs were weighted $w = 0.5$, the external edges were weighted 1, and the eigenvalues were calculated. It was found that each of these molecules has half positive and half negative eigenvalues, in agreement with Conjecture 2.10. The data is presented in Table 1.

It is easy to see that there is a single saturated hydrocarbon with 5 atoms, and none with 6 atoms. There is a unique saturated hydrocarbon with 7 atoms, pictured in Figure 6, along with a representation of its stellation.
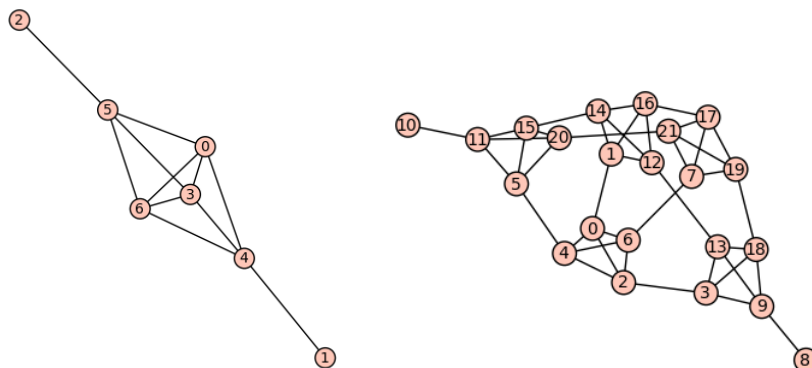
FIGURE 6. The graph on the left is the unique saturated hydrocarbon with 7 atoms. Its stellation is on the right. With internal weight $w = 0.5$, the eigenvalues are (approximately) 2.46, 1.94, 1.72, 1.72, 1.62, 0.72, 0.69, 0.5, 0.5, 0.5, 0.5, -0.5, -0.72, -0.72, -0.79, -1.27, -1.36, -1.5, -1.5, -1.5, -1.5, -1.5.

n	Number of connected graphs with $\Delta \leq 4$	Number of Saturated Hydrocarbons
5	21	1
6	78	0
7	353	1
8	1,929	5
9	12,207	12
10	89,402	44
11	739,335	190
12	6,800,637	995
13	68,531,618	6,211
14	748,592,936	45,116

TABLE 1. All counts are for non-isomorphic graphs.

4. CONCLUDING OVERVIEW

Here a simple model for saturated hydrocarbons has been described, and some first general features established, to reveal what every chemist "knows"—that alkanes are "stable", which in the present language and model is to say that the MO eigenvalues are divided with half positive and half negative. This result then is not surprising—but rather serves as an example to indicate that further general mathematical results might well be achievable for this class of molecules, which offers immensely greater number of examples, than does the class of benzenoids.

The model utilized here has been described as arising in the early decades of quantum chemistry. But it is somewhat amusing to note that the model we use has some even earlier precedents—van't Hoff's model [25] has in effect the external edges compressed to points. Also Sylvester's [24] molecular graphs (of 1878) look much like our stellated ones (though he seems to make a seeming "mistake" in including only four out of the six internal bonds for each C atom) presumably Clifford's [3, 4] model is also similar (though there seems to be a less complete description). Arguably these models may be viewed to involve a Clifford-algebraic (antisymmetric) pairing for each external bond—not too unlike the later localized-bonding VB model for the saturated hydrocarbons—something that would not take definitive form for another half century. This in some sense disagrees with Biggs, Lloyd, and Wilson's statement [1] that Sylvester's chemical ideas "went nowhere". Instead, these early ideas would give rise to the naming of mathematical "graph theory" and ultimately rather indirectly facilitate chemical graph theory. But also with Gordon and Alexejeff (who also thought of molecular modelling [11]) and Clifford there was a development of representation theory for groups and group algebras such as would ultimately enable the fundamental valence-bond theoretic descriptions [21, 17, 18] of molecular structure—see particularly Weyl's discussion [26, Appendix D]. Simply put, these early mathematicians[1] needed the vehicle of quantum mechanics to make sense of their molecular ideas. Here though a MO model approach for our saturated hydrocarbons has been taken, a VB-theoretic development could also be imagined to be worthwhile.

Further, extension of the current work can be imagined. Development of our simple model to understand the cycle-containing saturated hydrocarbons would be of value. Also elaboration of the eigenvalue distribution (as a function of structure) could be of value, particularly as regards the gap around 0. Yet also extensions to deal with the case that the H- and C- atom orbitals are weighted differently would be of value. And even further, hetero-atoms might be allowed in the carbon network— one can imagine that rather general mathematical statements might be made via a perturbed-MO approach, like that practiced [6] in the context of ordinary Hückel theory. Indeed this approach should prove useful to account for the difference between the site weights for C and H orbitals—the hetero-atom weights so treated in this conventional perturbed MO theory being more significant than for our present case (of C and H). Thence it seems that there remains much promise for chemical

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[1]Amongst these "early mathematicians" one might also be tempted to include A. A. Cayley for his somewhat more widely recognized work on alkane enumeration [2]. But though he evidently learned of this matter from Sylvester [24], Cayley stuck with the ordinary molecular graph (as in Figure 1), or yet more abbreviatedly with the H-deleted C-network graph.

graph theory, even in the context of understanding electronic structure in a general way. See, also [15] for an even somewhat broader discussion of such prospects.

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