Eigenvalues of Saturated Hydrocarbons

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- captures what every chemist "knows"—that alkane MO eigenvalues are half positive and half negative,
- suggesting that further mathematical results for this class are achievable,
- and using chemical graph theory to describe the electronic structure of molecules other than conjugated hydrocarbons.

Saturated Hydrocarbons

Definition

A *saturated hydrocarbon* is a connected graph whose vertices have both degrees one and four and no other degrees.

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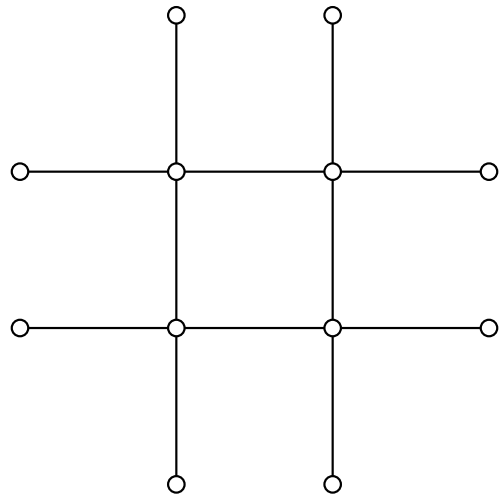

Figure: Cyclobutane C_4H_8.

Alkanes

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An *alkane* is an acyclic saturated hydrocarbon.

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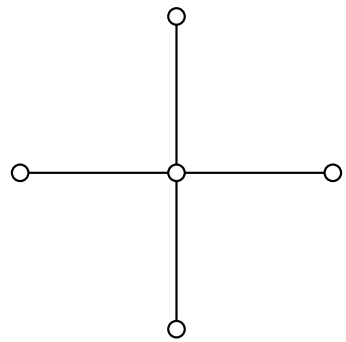

Figure: Methane CH_4.

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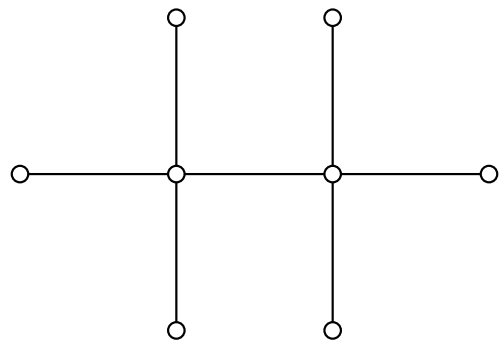


Figure: Ethane C_2H_6.

n	Connected graphs with $\Delta \leq 4$	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: All counts are for non-isomorphic graphs.

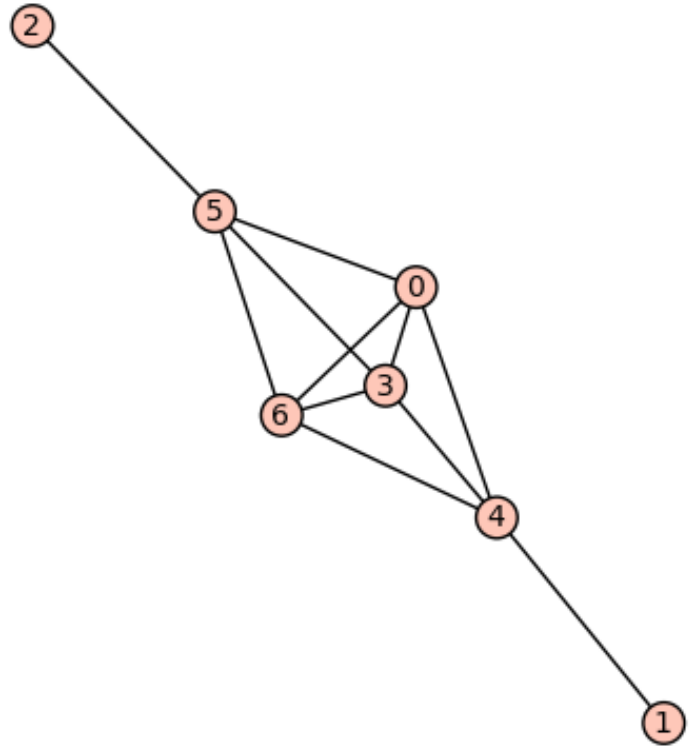
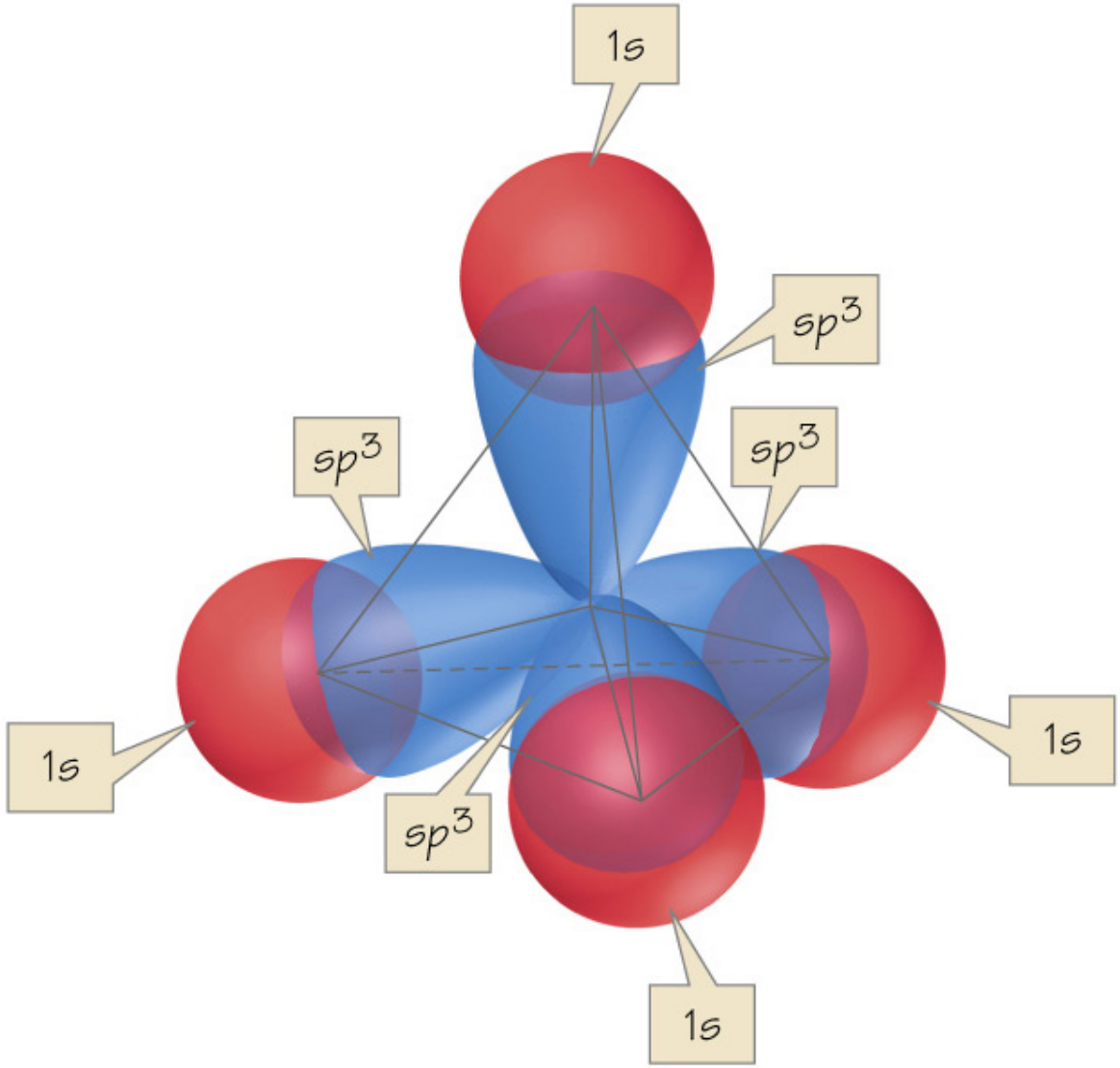


Figure: The unique saturated hydrocarbon with 7 atoms.

Molecular Orbitals



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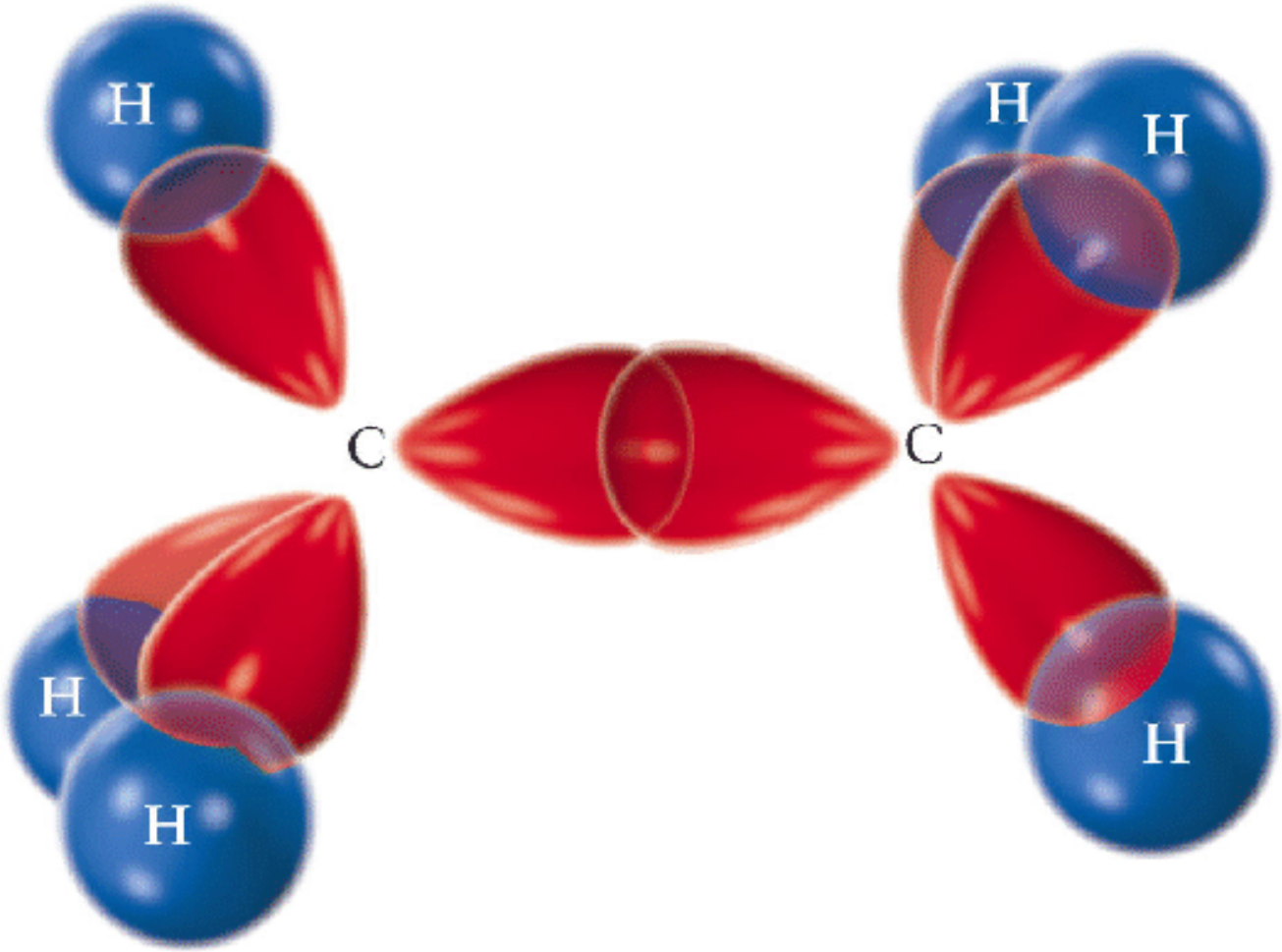

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The Stellation Model

Definition

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 $E^*_{ext} = \{(a,b)(b,a) : a \sim b \text{ in } G\}$,
- $E^*_{int} = \{(a,b)(a,c) : a \sim b \text{ and } a \sim c \text{ in } G\}$, and
- $E(G^*) = E^*_{int} \cup E^*_{ext}$.

The Stellation Model

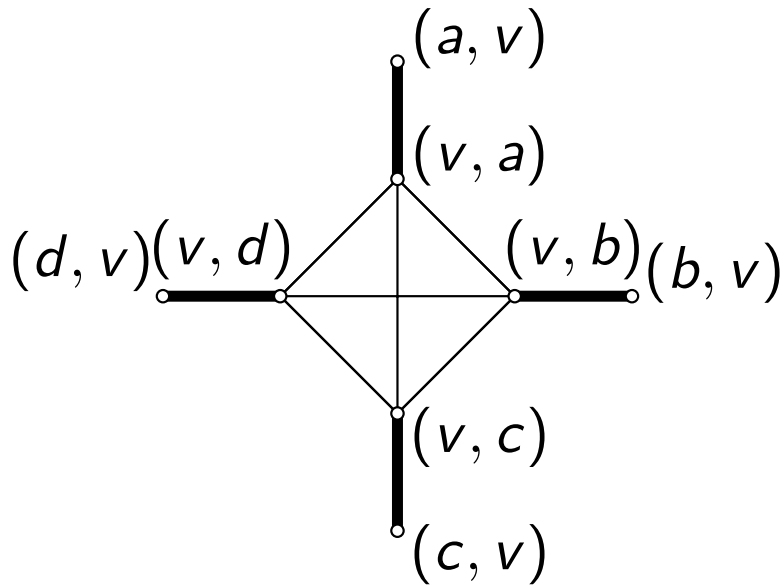

Figure: The stellation G^* of methane CH_4.

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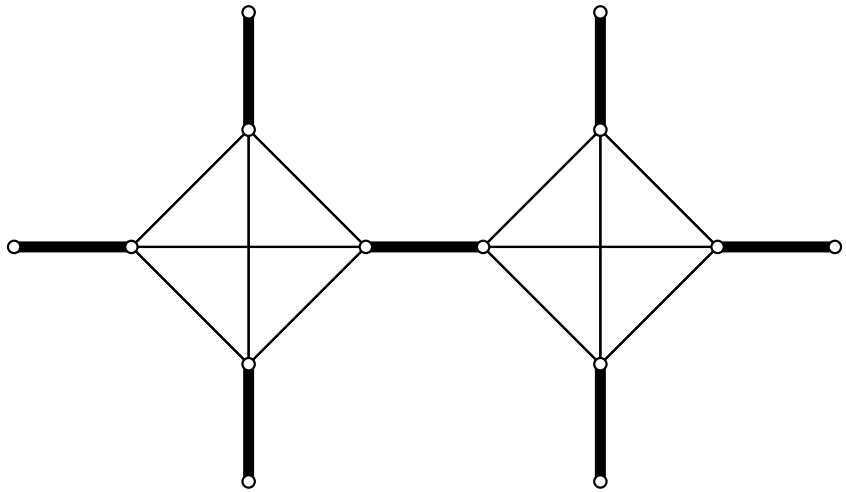

Figure: The stellation G^* of ethane C_2H_6.

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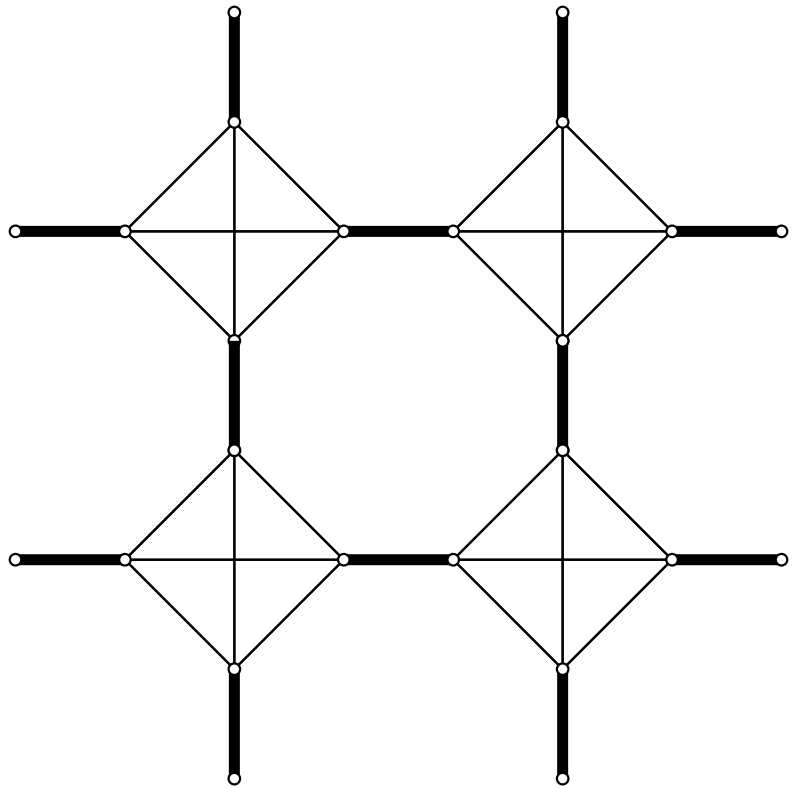

Figure: The stellation G^* of cyclobutane C_4H_8.

Some Precursers

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From the Chemical Literature:

- C. Sandorfy, *LCAO MO calculations on saturated hydrocarbons and their substituted derivatives*, Canadian Journal of Chemistry **33** (1955), no. 8, 1337–1351.
- K. Fukui, H. Kato, and T. Yonezawa, *Frontier electron density in saturated hydrocarbons*, Bulletin of the Chemical Society of Japan **34** (1961), no. 3, 442–445.
- J. A. Pople and D. P. Santry, *A molecular orbital theory of hydrocarbons*, Molecular Physics **7** (1964), no. 3, 269–286.

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From the Mathematical Literature:

- Schmidt & Haynes, 1990, Dunbar & Haynes, 1996, Favaron, &c.
- T. Shirai, *The spectrum of infinite regular line graphs*, Transactions of the American Mathematical Society **352** (2000), no. 1, 115–132.

A Property of Stellated Graphs

The external edges form a perfect matching.

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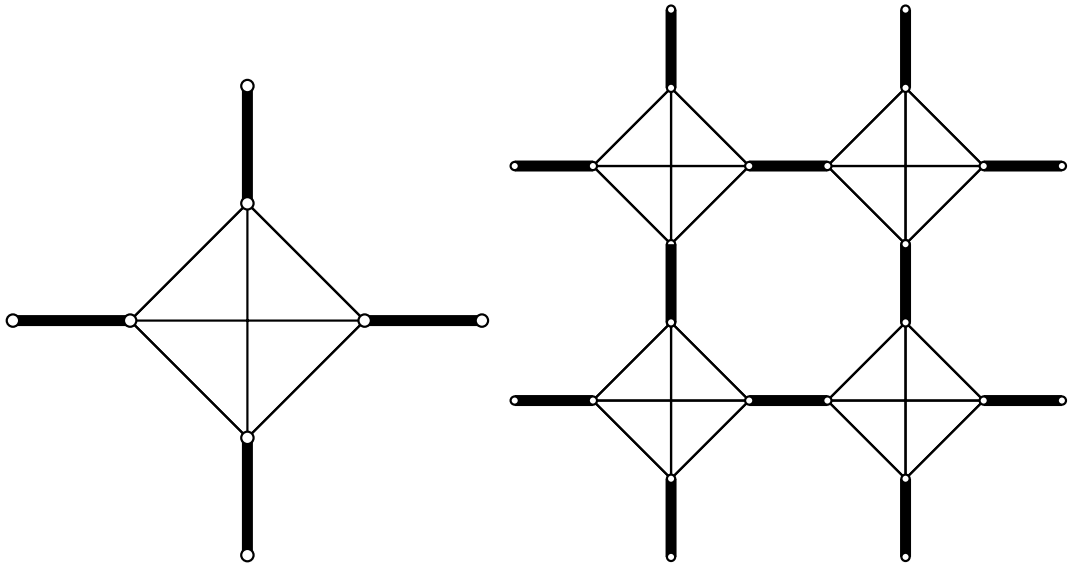

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For a stellated graph G^* with vertex set $V(G^*) = \{v_1, \ldots, v_n\}$ we define a weighted adjacency matrix A^w as follows:

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A^w is the *weighted adjacency matrix* for G^*.

The Determinant

Definition

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.

The Main Lemma

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If $\det A^w \neq 0$ for all $w \in I$ then A^w has half positive and half negative eigenvalues for each $w \in I$.

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Theorem

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

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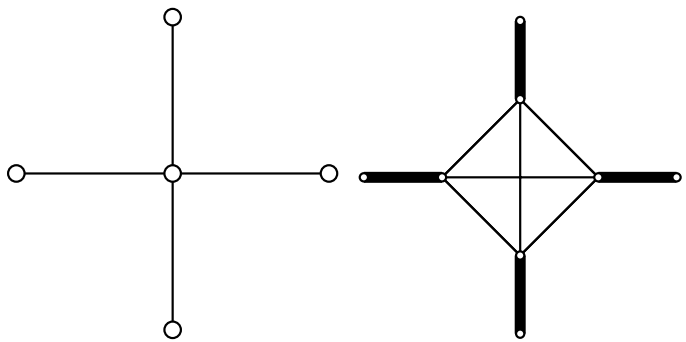

Unicyclic Saturated Hydrocarbon Eigenvalues

Lemma

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

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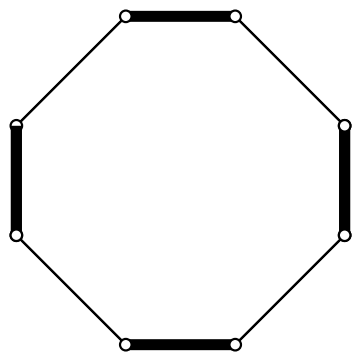

Unicyclic Saturated Hydrocarbon Eigenvalues

Lemma

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.

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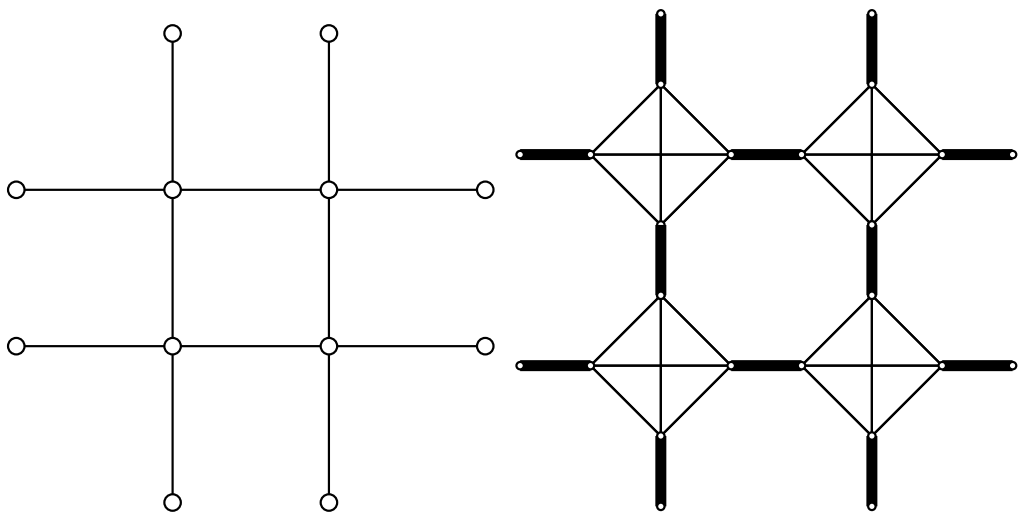

Unicyclic Saturated Hydrocarbon Eigenvalues

Theorem

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

A General Theorem

Theorem

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* $c > 0$.

A Conjecture

Conjecture

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.*

Thank You!

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D. J. Klein and C. E. Larson,
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