#### **HOMO-LUMO MAPS AND GOLDEN GRAPHS**



#### Tomaž Pisanski, Slovenia CSD5, Sheffield, England Wednesday, July 21, 2010

#### Outline – HOMO-LUMO maps

- Recently, we introduced a graphical tool for investigating spectral properties of graps that we caled **HOMO-LUMO maps**. On a HOMO-LUMO map a graph G is represented by point with  $(\lambda_h, \lambda_l)$  coordinates, where , roughly speaking  $\lambda_h$  and  $\lambda_l$  are the two middle eignevalues of G.
- The difference  $(\lambda_h \lambda_l)$  is the well-**known HOMO**-**LUMO gap** in Hueckel theory. Therefore it is surprising that although the middle eigenvalues have clear significance in mathematical chemistry not much attention has been paid to them in spectral graph theory.

#### Outline- Golden Graphs

It turns our that the HOMO-LUMO maps are well suited tool in investigating families of graphs, such as molecular trees, fullerenes, etc., where extremal points or appearing patterns raise interesting questions. For instance, for small molecular graphs the HOMO-LUMO plot clearly shows that the vertical line  $\lambda_{\rm h} = 1/\phi$ , where  $\phi$  is the golden ratio, is heavily populated. We call graphs with  $\lambda_{\rm h} = 1/\phi$  golden graphs. We present some results and raise some questions that resulted from the study of HOMO-LUMO maps.

#### References

- 1. P.W. Fowler, T. Pisanski, HOMO-LUMO maps for chemical graphs, MATCH Commun. Math. Comput. Chem., 64 (2010) 373-390.
- 2. P.W. Fowler, T. Pisanski, HOMO-LUMO maps for fullerenes, Acta Chim. Slov., In press, 2010.

# Golden graphs or Golden HOMO graphs?

- Ernesto Estrada: I just want to mention that the name "golden spectral graphs" and "golden graphs" have been introduced by myself in 2007. I am attaching a new paper on this topic which is now in press in Automatica with the definition and some properties of golden graphs. I think that to avoid confusions it would be better if you can call your graphs "golden HOMO-LUMO" ones instead of golden graphs.
- Estrada, E. (2007). Graphs (networks) with golden spectral ratio. *Chaos, Solitons and Fractals, 33, 1168-1182.*

# Graph spectrum



- Recall the definition of graph spectrum.
- Let G be a graph on n vertices and A(G) its adjacency matrix.
- The collection of eigenvalues of A(G) is called the **spectrum** of G.
- Since A(G) is symmetric matrix the spectrum is real and can be described as follows:

$$\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_n$$

### Spectral radius



- Spectral radius:
  - $\rho(G) = \max |\lambda_i|$
  - λ<sub>1</sub> is called the leading or principal eigenvalue.
  - We may consider a disk centered in the origin of the complex plane which covers all eigenvalues and has the least possible radius.

## Some properties

- **Proposition 1.** Graph spectrum is real and is a graph invariant.
- **Proposition 2**. (max valence bound )  $\Delta(G) \ge \rho(G)$ .
- **Proposition 3.**  $\lambda_1 = \rho(G)$ .
- **Proposition 4**.  $\lambda_1 \ge 2m/n = d$  (average valence).
- **Theorem 5**. Spectrum is symmetric if and only if the graph is bipartite.
- **Theorem 6**. If G is regular of valence d then  $\rho(G) = d$ .

# HOMO-LUMO gap

- In addition to principal eigenvalue other eigenvalues have been studied in chemical graph theory (minimal, second one, ...).
- We are interested in the middle eigenvalues. For even n this is well-defined.
- Define H = n/2 and L = 1 + n/2.
- If n is odd, we define H = L = (n+1)/2.
- . In chemical graph theory the eigenvalue difference  $~\lambda_{H}$   $\lambda_{L}$  is called the **HOMO-LUMO gap** of G.

## Chemical graphs

- G is a **chemical graph** if
  - It is connected
  - Its max valence is at most 3:  $\Delta(G) < 4$ .
- Motivation from chemistry:
  - Chemical graphs model fully conjugated  $\pi$ -systems.
    - Vertex Carbon atom
    - Edge σ-bond (= overlap of two adjacent sp2 - orbitals)
    - There are n delocalized  $\pi$ -orbitals.

#### $\sigma$ -bonds and $\pi$ -bonds



- A several step process:
- 1. 4 orbitals per C atom (2s,2px,2py,2pz)
- 2. 3 hybrid sp2 orbitals (+ one pure pz orbital)
- 3. A pair of adjacent hybrids forms a  $\sigma$ -bond
- 4. A pair of adjacent p-orbitals forms a  $\pi$ -bond accomodating two electrons.
- 5. Alternative: Pz electrons are delocalized and move in eigenspaces of the adjacency matrix.

## Simple Hückel model

- chemical graph
- eigenvalue
- eigenvector
- positive eigenvalue
- negative eigenvalue
- assignment of tags to eigenvectors.
- number of tags
- eigenvector with two tags
- eigenvector with one tag
- eigenvector with no tags
- eigenvector belonging to an eigenvalue with multiplicity > 1.

- molecular graph of fully πconjugated system.
- orbital energy
- molecular orbital
- bonding orbital
- anti-bonding orbital
- electron configuration
- number of  $\pi$ -electrons
- fully occupied orbital
- partially occupied orbital
- unoccupied orbital
- degenerate orbital

# Electronic configuration of a graph

- Let G be a graph.
- Vector  $\mathbf{e} = (e_1, e_2, \dots, e_n)$  with  $e_i$  from  $\{0, 1, 2\}$
- is called an **electronic configuration**
- with k electrons on G if  $\Sigma e_i = k$ .
- In this paper we consider only the case k = n.

# Ground-state electronic configuration

- Electronic configuration may be
  - ground-state configuration
  - excited-state configuration
- Ground-state configuration is completely determined by the following principles:
  - Aufbau principle
  - Pauli principle
  - Hund's rule
- Note: In simple Hückel model ground-state configuration is completely determined by the graph. This means that this concept is a graph invariant.

#### Aufbau Principle



• Fill orbitals in order of decreasing eigenvalue.

#### Pauli Principle

![](_page_15_Figure_1.jpeg)

• No orbital may contain more than two elecrons

# Hund's Rule of Maximum Multiplicity

![](_page_16_Figure_1.jpeg)

• No orbital receives the second electron before all orbitals degenerate with it have each received one.

# HOMO- LUMO

- Eigenvector with two tags belonging to the smallest eigenvalue.
- Eigenvector with no tags belonging to the largest eigenvalue.
- The difference of the corresponding eigenvalues.

- HOMO Highest
   Occupied Molecular
   Orbital
- LUMO Lowest
   Unoccupied Molecular
   orbital
- HOMO-LUMO gap: the energy difference of the corresponding molecular orbitals

# HOMO-LUMO gap

![](_page_18_Figure_1.jpeg)

- HOMO Highest
   Occupied Molecular
   Orbital
- LUMO Lowest
   Unoccupied Molecular
   Orbital

# Existence of partially occupied orbitals

- There is no problem with the HOMO-LUMO gap if there are no partially occupied orbitals.
- Partially occupied orbitals may arise for two reasons.
  - n is odd.
  - n is even or odd but there are partially occupied molecular orbitals arising from Hund's rule.
- In any case, if there are partially occupied orbitals, they all have the same energy level.
- In this case the definition of HOMO and LUMO has to be amended.
- If there exists a partially occupied orbital it is both HOMO and LUMO (SOMO) and the HOMO-LUMO gap is 0.

# Closed-shell vs. Open-shell molecules

- A well-known concept in mathematical chemistry is the idea of an **open-shell** vs. **closed-shell** molecule.
- It has been refined (see Fowler, Pisanski, 1994)
   to
  - properly closed
  - pseudo closed
  - . meta closed
- One could give an algebraic definition for these concepts, but ... we turned to geometry

### HOMO-LUMO map

![](_page_21_Figure_1.jpeg)

- The pair of HOMO-LUMO eigenvalues  $(\lambda_{HOMO}, \lambda_{LUMO})$  may be represented as a point in a plane.
  - For a family of graphs Γ we get a set of points.
  - Such a diagram in the HOMO-LUMO plane is called the **HOMO-LUMO map** of Γ.

# Regions in HOMO-LUMO maps

![](_page_22_Figure_1.jpeg)

- A well-known concept in mathematical chemistry is the idea of an **open-shell** vs.
   **closed-shell** molecule.
- It has been refined as shown on the left (see Fowler, Pisanski, 1994) to
  - properly closed
  - pseudo closed
  - . meta closed

# Regions in HOMO-LUMO maps

![](_page_23_Figure_1.jpeg)

- Note: Open-shell is the same thing as HOMO-LUMO gap is 0.
- Note: The region above the open-shell line is never attained in the ground state.
- Recently we extended the definition to
  - properly open
  - . pseudo open
  - meta open

# Lines in a HOMO-LUMO map

![](_page_24_Figure_1.jpeg)

- Some important lines:
  - y = x (open-shell)
  - y = -x (balanced)
- If two points lie on the same lines the graphs are called:
  - isohomal (vertical)
  - isolumal (horizontal)
  - **isodiastemal** (y = x +c, same

HOMO-LUMO gap).

### Pseudo-bipartite graphs

![](_page_25_Figure_1.jpeg)

- All bipartite graphs are **balanced**.
- However, there exist non-bipartite balanced graphs. We call such graphs pseudobipartite.
- balanced = bipartite
  + pseudo-bipartite

#### Chemical triangle

![](_page_26_Figure_1.jpeg)

The right triangle with vertices (-1,-1),(1,-1),(1,-1) is called the chemical triangle.

#### Conjecture

![](_page_27_Figure_1.jpeg)

- The right triangle with vertices (-1,-1),(1,-1),(1,-1) is called the chemical triangle.
- **Conjecture:** Each chemical graph is mapped in the chemical triangle.

### The Heawood graph

![](_page_28_Picture_1.jpeg)

- The Heawood graph is the only known counterexample to the conjecture.
- Levi graph (= incidence graph) of the Fano plane
- 6-cage
- 7 hexagonal regions on torus. Proof that maps on torus require up to 7 colors.

# Hückel Energy

- Total energy of  $\pi$ -system may be approximated by the energy of an electronic configuration **e**:
- HE(G,**e**) =  $\Sigma e_i \lambda_i$ .
- For a ground-state electronic configuration we get the **Hückel energy** of a graph:
- HE(G) =  $2(\lambda_i + \lambda_2 + \dots + \lambda_{n/2})$ , if n even.
- HE(G) =  $2(\lambda_i + \lambda_2 + \dots + \lambda_{(n-1)/2}) + \lambda_{(n+1)/2}$  if n odd.

# Energy of a graph

- The concept of graph energy E(G) was introduced by Ivan Gutman in the 70's as the sum of absolute values of its eigenvalues.
- $E(G) = \Sigma | \lambda_i |$ .
- In general E(G) HE(G). For bipartite graphs the equality holds.
- If G has n vertices and m edges then the following are true:
  - **Proposition 7**:  $0 = \Sigma \lambda_i$ ,
  - **Proposition 8:**  $2m = \Sigma |\lambda_i|^2$ ,
- **Proposition 9.**  $E(G) \ge 2\lambda_1$
- **Proof:** By Propsition 7, the sum of all positive eigenvalues add up to E(G)/2. Hence  $E(G)/2 \ge \lambda_1$  and the result follows.

#### Comb

![](_page_31_Figure_1.jpeg)

- Comb(p) is a tree on
   n = 2p vertices.
- Vertices: u<sub>i</sub>, v<sub>i</sub>.
- Edges:  $u_i \sim v_i$ . and  $u_i \sim u_{i+1}$ .

#### Conjecture holds for trees

- **Theorem 10:** All chemical trees are mapped into the chemical triangle.
- **Proof**: In 1999 Zhang and An proved that among all chemical trees *combs* have maximal HOMO-LUMO gap. In 2001 Fowler, Hansen, Caporossi and Soncini determined the eigenvalues of a comb with n=2p vertices. From their result it follows that
- $\lambda_{HOMO} = \lambda_p = \cos(\pi p/(p+1)) + (1 + \cos(\pi p/(p+1)))^{1/2}$
- Clearly  $2^{1/2} 1 \le \lambda_p \le 1$ . Since trees are bipartite graphs  $\lambda_{LUMO} = -\lambda_{HOMO}$  the result follows.

#### Anti-spectral Radius

![](_page_33_Figure_1.jpeg)

- Motivated by the notion of spectral radius, as the smallest radius centered at the origin that covers the whole spectrum we define the HOMO-LUMO radius r(G) as the largest radius that misses the spectrum. (It must hit at least one eigenvalue).
  - $r(G) = min\{|\lambda_i|\}$
  - For a properly closed graph this would be  $r(G) = \min{\{\lambda_{H}, -\lambda_{L}\}}$

#### An Observation

 Note that graph G is singular if and only if its antispectral radius is zero: r(G) = 0. If at the same time R(G) > 0, G must be either pseudo or meta.

# HOMO-LUMO Radius

![](_page_35_Figure_1.jpeg)

• We define the third radius R(G) as the smallest radius of a disc tcontered in the origin that covers both HOMO and LUMO eigenvalue and we call it the **HOMO-LUMO radius**:

$$R(G) = max\{|\lambda_{H}|, |\lambda_{L}|\}$$

- **Proposition 11:** For all graphs  $r(G) \le R(G)$ . The equality holds if and only if G is properly closed (or properly open).
- We may now restate our conjecture:
- For each chemical graph
  - $R(G) \leq 1$ .

#### Two results

- Theorem 12: Let G be a properly closed graph of average valence d. Then its HOMO-LUMO radius R(G) is bounded: R(G) ≤ 2sqrt(d).
- Theorem 13: Let G be a balanced graph of average valence d. Then its HOMO-LUMO radius R(G) is bounded: R(G) ≤ sqrt(d).
- The proof of both results follows from the following Lemmata.

#### McClelland's Lemma

- We give a short independent proof of McClelland's lemma.
- Lemma 14:  $E(G) \leq sqrt(2mn)$ .
- **Proof:** Apply the well-known fact that the quadratic mean is greater or equal to the arithmetic mean to the absolute values of n eigenvalues of G we obtain:
  - $\operatorname{sqrt}((1/n) \Sigma |\lambda_i|^2) \ge (1/n) \Sigma |\lambda_i|$
- Using  $2m = \Sigma |\lambda_i|^2$  and  $E(G) = \Sigma |\lambda_i|$ , we obtain
  - $sqrt(2m/n) \ge E(G)/n$  and therefore  $E(G) \le sqrt(2mn)$ .

#### Lemma

- Lemma 15: Let G be a properly closed graph of average valence d = 2m/n. Then  $(\lambda_H \lambda_L)/2 \le sqrt(d)$ .
- **Proof**: In the properly closed case the minimum  $\min\{|\lambda_i|\}$  is attained by HOMO- or LUMO-eigenvalue. More precisely, H is the index of the smallest positive and L the index of the largest negative eigenvalue. Therefore  $E(G) = \sum |\lambda_i| \ge n(\lambda_H \lambda_L)/2$ .
- Since d = 2m/n, by McClelland's Lemma we may derive:
- $n \operatorname{sqrt}(d) = \operatorname{sqrt}(2mn) \ge E(G) \ge n(\lambda_H \lambda_L)/2.$
- The resulting inequality follows readily.

# Proofs

![](_page_39_Figure_1.jpeg)

- The area above the skew line satisfies Lemma 15.
  - Proof of Theorem 12:
    Follows directly from
    Lemma 15 In this case
    R is determined by the
    dotted red line..

#### Proof of Theorem 13:

All balanced graphs (green line) are proper, hence Lemma 15 applies. In this case R is determined by the blue line.

#### Some Problems

- **Problem 1**. How sharp are the bounds of Theorems 12 and 13?
- **Problem 2**. Does there exist a constant K such that R(G) < K, for any graph G?
- **Problem 3**. Determine the family of graphs for which HE(G) = E(G).

# Graphs outside chemical triangle

![](_page_41_Figure_1.jpeg)

 Gašper Jaklič, Patrick Fowler and TP found several infinite families of (nonchemical) graphs outside chemical triangle with the property that R(G) tends to infinity.

## Graphs with maximal value of R

- Among graphs on n vertices, the ones maximizing R are:
- $n = 6 \dots$  Five-sided pyramid. (Wheel with 5 spokes)
- $n = 8 \dots$  Twodimensional subdivision of tetrahedron.
- $n = 10 \dots$  Complement of the Petersen graph
- **Problem 4.** Determine extremal n-graphs with respect to R.
- **Problem 5**. Determine extremal (n,m)-graphs with respect to R.

#### Some computer experiments

![](_page_43_Figure_1.jpeg)

- The Wheels (or pyramid graphs)
- Clear distinction
   between odd number of vertices and even number of vertices.
- Meta open and properly closed
- One golden example

![](_page_44_Figure_1.jpeg)

• Cartesian product

• 
$$C_n \ge K_2$$

![](_page_45_Figure_1.jpeg)

- Cartesian product
- $C_n \ge K_3$
- No properly closed example?

![](_page_46_Figure_1.jpeg)

![](_page_47_Figure_1.jpeg)

#### Division lines

• Visible division lines that partition the map into regions. • Each region should be studied separately.

# Golden graphs

- On the left, there is a clearly visible vertical line at
- $\lambda_{\rm H} = 1/\phi$  ,
- where  $\phi$ . is the golden section  $_{\circ}$  $\phi = (1 + \text{sqrt}(5))/2 \text{ and } 1/\phi = 1$  $-\phi$ .
- A graph with  $\lambda_{\rm H} = 1/\phi$  is called **a golden graph**.
- Some other visible lines:

• 
$$\lambda_{\rm H} = 0$$
,  $\lambda_{\rm L} = -1$ ,  $\lambda_{\rm H} = \lambda_{\rm L} \lambda_{\rm H} = -\lambda_{\rm L}$ .

![](_page_49_Figure_7.jpeg)

#### Some questions

- 1. Why is the reciprocal golden ratio visible in the HOMO-LUMO map? Is the visual impression that the density of points is a local maximum on this line indicative of some kind of 'attractor' behaviour, or just an artefact of small numbers?
- 2. Is it possible to characterize the family of golden graphs, or of golden chemical graphs?
- 3. Do chemical golden graphs have any common physical or chemical property? In the very simplest version of the Huckel approximations, all would have a common ionisation energy of  $0.618...\beta$ , or around  $1.5 \text{eV}^4$
- 4. There are some well-known graphs, such as path  $P_4$  or cycles  $C_5$ ,  $C_{10}$  that are golden. Are there any known infinite families of golden graphs?
- 5. Which benzenoid graphs are golden? Benzene itself is not golden, but naphthalene is.
- 6. Which fullerene<sup>5</sup> graphs are golden? It appears that only a few fullerenes have  $\lambda_H = \phi^{-1}$ . Computer search up to n = 140 finds only 5: these are  $32:6\;44:72$  50:263 50:270 and 60:1812 (in the spiral notation, where fullerenes are ordered by their canonical face spirals).

#### Two more questions

- 7. Among non-bipartite chemical golden graphs, it appears that most examples contain a cycle of length 5. Is the number of such graphs without a 5-cycle finite?
- 8. Is the number of chemical golden graphs finite? Given that the spectrum must 'fit' in the interval +3 to -3, and must accommodate more levels as n increases, does the HOMO eigenvalue at  $\phi^{-1}$  get 'crowded out'?

#### Some golden graphs

- Path P<sub>4</sub>
- Cycles  $C_5$ ,  $C_{10}$ .
- The graph below is non-bipartite with no pentagons.

![](_page_52_Picture_4.jpeg)

 Some bipartite golden graphs

![](_page_52_Figure_6.jpeg)

#### Golden chemical graphs

![](_page_53_Picture_1.jpeg)

 Here are all 23 golden chemical graphs for n < 10.</li>

Figure 4: Small golden chemical graphs up to n = 9.

# Missing graph

• There are only 22 graphs. No. 11 is missing.

![](_page_54_Picture_2.jpeg)

# Small non-chemical golden graphs

![](_page_55_Figure_1.jpeg)

Figure 3: Up to n = 7 there are only four connected golden graphs that are not chemical.

# How many benzenoids are golden?

- Is naphthalene the only golden benzenoid?
- Are there infinitely many bipartite golden chemical graphs?

![](_page_56_Figure_3.jpeg)

#### Golden Fullerenes

• Patrick Fowler

discovered 5 golden fullerenes:

- n = 32,40,50,50,60.
- Note:
  - Most numbers divisible by 5.
  - Two on 50 vertices
  - C60 –

buckminsterfullerene!

- **Conjecture:** There are only 5 golden fullerenes.
- Search for other golden polyhedra:
- **Conjecture:** There are no other golden polyhedra.

#### Golden chemical graphs

<b>#vertices</b>	<b>#ch graphs</b>	#golden ch g
2	1	0
3	2	0
4	6	1
5	10	1
6	29	6
7	64	1
8	194	12
9	531	2
10	1733	47
11	5524	5
12	19430	206
13	69322	10
14	262044	740
15	1016740	57
16	4101318	3913

Number of chemical graphs and number of golden chemical graphs on n vertices, n = 1, 2, ..., 16.

#### The Five Golden Fullerenes

44:72

![](_page_59_Picture_2.jpeg)

![](_page_59_Picture_3.jpeg)

 Among the five golden fullerenes it is also the largest: C60 – Buckminster Fullerene

50:270

![](_page_59_Picture_6.jpeg)

![](_page_59_Picture_7.jpeg)

60:1

![](_page_59_Picture_9.jpeg)

#### An interesting twist

- In June 2010 Roger Blakeney Mallion
   pointed out an interesting
   phenomenon that may occur in certain open shell graphs.
- R.B.Mallion, D.H.Rouvray: Molecular Topology and the Aufbau Principle, Mol. Phys. 36(1978) 125–128.
- R.B.Mallion, D.H.Rouvray: On a new index for characterising the vertices of certain non-bipartite graphs, Studia Sci. Math. Hungarica 13(1978) 229– 243.
- R.B. Mallion: An analytical illustration of the relevance of molecular topology to the Aufbau process, CCA 56 (1983) 477–490.

![](_page_60_Figure_5.jpeg)

![](_page_60_Figure_6.jpeg)

#### Jahn-Teller Graphs

# vertices	# graphs
2	0
3	1
4	1
5	8
6	10
7	206
8	473
9	30900

**JT graph**: open-shell with k SOMO orbitals occupied in total by s electrons, such that

1.  $1 \delta s \leq 2k-1$ 

$$2. \quad s \neq k.$$

<sup>3.</sup> There are two cases:

- s < k (each orbital is either empty or has one electron)
- s > k (each orbital has either one or two electrons)

#### Jahn-Teller Molecular Graphs

# vertices	#molecular graphs	
2	0	
3	1	
4	1	
5	1	
6	0	
7	7	
8	1	
9	34	
10	14	
11	357	
12	185	
13	4456	
14	2885	

#### Announcements

![](_page_63_Picture_1.jpeg)

#### Ars Mathematica Contemporanea publishes papers in Mathematical Chemistry (or Chemical applications of Mathematics)

**Bled 2011** (7<sup>th</sup> Slovenian International Conference in Graph Theory) will take place 19 – 25 June 2011.

![](_page_64_Figure_0.jpeg)

 CSD 6 will take place in Slovenia in 2012. It will be organized by Klavdija Kutnar and Tomaž Pisanski. Details will be available at the Bled meeting in 2011.