

Scientific paper

HOMO-LUMO Maps for Fullerenes

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This paper is dedicated to Professor Milan Randić on the occasion of his 80th birthday

Abstract

The HOMO-LUMO map is found to be a useful tool for classifying π -electron configurations of fullerenes and identifying research questions about their adjacency spectra.

Keywords: Fullerenes, Hückel molecular orbital theory, graph theory, HOMO, LUMO

1. Introduction: the HOMO-LUMO Map

The HOMO-LUMO map has been proposed as a qualitative tool for the study of trends in π -electronic configurations for conjugated systems modelled by various classes of chemical graphs.¹ The idea is to make a scatterplot of Hückel HOMO vs LUMO eigenvalues and investigate the clustering of the results. In Ref.1, the maps suggested a theorem for eigenvalue bounds on chemical trees, and a conjecture for more general chemical graphs. Here, we use this simple device to re-examine some aspects of the qualitative theory of the electronic structure of fullerenes and identify some plausible conjectures.

In the simple Hückel model, eigenvectors and eigenvalues of the adjacency matrix of the molecular graph of a π -conjugated system correspond to π molecular orbitals and their energies (in units of $|\beta|$, with respect to an origin at α). The eigenvalues are arranged in non-decreasing order and, as fullerenes are non-bipartite cubic graphs, they run from $\lambda_1 = +3$ to $\lambda_n > -3$. Occupation of the orbitals in the electronic ground state is determined by the usual trinity of Aufbau and Pauli Principles and Hund's Rule of Maximum Multiplicity. The HOMO is the non-empty orbital of highest energy² and for graphs with even n and no net charge has eigenvalue equal to $\lambda_{n/2}$; the LUMO is the non-fully occupied orbital of lowest energy² and for graphs with even n and no net charge has eigenvalue equal to $\lambda_{(n/2)+1}$; if the system has partially occupied orbitals, HOMO and LUMO have equal eigenvalues.

It is usual to divide electron configurations into open and closed shells, but a finer classification can be useful. The six classes based on the HOMO and LUMO eigenvalues are three closed and three open:

- (i) If all orbitals contain either zero or two electrons, the system is a closed shell, and belongs to one of three sub-classes:³
 - (ia) *Pseudo-closed*: $\lambda_{\text{LUMO}} > 0$,
 - (ib) *Properly closed*: $\lambda_{\text{HOMO}} > 0 \geq \lambda_{\text{LUMO}}$,
 - (ic) *Meta-closed*: $\lambda_{\text{HOMO}} \leq 0$.
- (ii) If there is at least one orbital that is partially occupied the configuration is an open shell, and belongs to one of three sub-classes:¹
 - (iia) *Pseudo-open*: $\lambda_{\text{HOMO}} = \lambda_{\text{LUMO}} > 0$,
 - (iib) *Properly open*: $\lambda_{\text{HOMO}} = \lambda_{\text{LUMO}} = 0$,
 - (iic) *Meta-open*: $\lambda_{\text{HOMO}} = \lambda_{\text{LUMO}} < 0$.

2. Fullerenes and HOMO-LUMO Maps

Fullerenes are polyhedral carbon cages C_n with 12 pentagonal and $(n/2 - 10)$ hexagonal faces. Since the discovery of the first example, C_{60} ,⁴ they have been the subjects of intense experimental, theoretical and mathematical interest.⁵ Fullerenes are mathematically possible for $n = 20$ and all even values $n \geq 24$, and as n increases the number of possible isomers grows rapidly,⁶ though only a small subset of these have been observed in experiment.

Some fullerenes have open shells (pseudo, proper and sometimes meta⁷), but the vast majority have closed shells. Of these, some are properly closed, but most are pseudoclosed.^{5,8} Three classes of properly-closed shell fullerenes are known. These are the leapfrogs, the carbon cylinders and the sporadic closed shells.

Leapfrog fullerenes C_n have molecular graphs that can be constructed from the graph of a fullerene $C_{n/3}$ with one third as many vertices by first capping every face (raising a pyramid on each face) and then taking the dual of the resulting deltahedral polyhedron.⁹ As fullerene graphs exist for all vertex counts $20 + 2h$ with $h \neq 1$, where h is the number of hexagonal faces, leapfrog fullerenes exist for all $n = 60 + 6h$ with $h \neq 1$, one leapfrog corresponding to each isomer of the smaller fullerene and where the total number of hexagons is now $3h + 20$. The construction separates the faces of the original fullerene, introducing new hexagons at all original vertices, and maintaining point-group symmetry. The first leapfrog fullerene is the experimental isomer of C_{60} , derived from the C_{20} dodecahedron. It has been proved that leapfrog fullerenes all have properly closed shells.¹⁰

Carbon cylinders¹¹ are derived by expansion of icosahedral C_{60} or its D_{6d} analogue C_{72} along the principal rotational axis. The resulting fullerene consists of a tubular graphene-like part, made of hexagons, capped in a unique way by hemispherical portions of the C_{60}/C_{72} parent. As successive layers of hexagons are added to the central portion, the caps alternate from mutually eclipsed to staggered positions. Addition of a single belt of five (six) hexagons leads to the D_{5h} isolated-pentagon isomer of C_{70} (D_{6h} isolated-pentagon isomer of C_{84}) with a properly closed shell in which a bonding HOMO lies below an exactly non-bonding LUMO. This pattern of HOMO and LUMO eigenvalues is repeated thereafter with every third insertion of a belt of hexagons, leading to a series of five- and six-fold symmetric cylindrical properly closed-shell fullerenes with vertex counts $10(7 + 3k)$ and $12(7 + 3k)$, respectively, where $k \geq 0$. The pattern is rationalised by considering surface harmonics.¹¹ The smallest carbon cylinder is the second-most abundant experimental fullerene, C_{70} . Five- and six-fold symmetric cylinders of equal k have equal HOMO eigenvalues¹¹ and hence appear at the same point on the HOMO-LUMO map.

These two classes account for all the known properly closed fullerene graphs up to 110 vertices. At 112 vertices, and at 116 vertices and beyond, some extra properly closed isomers are found, all with negative LUMO values of extremely small magnitude. All have low or trivial point-group symmetry, and in the range $112 \leq n \leq 140$ are known to have LUMO eigenvalues $0 > \lambda_{\text{LUMO}} > -0.03$ (A full list for this range is given in Table 3.2 of Ref.5). The distribution of sporadic isomers, with N the number at each order n , is:

| | | | | | | | | | | | | | | | |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| n | 112 | 114 | 116 | 118 | 120 | 122 | 124 | 126 | 128 | 130 | 132 | 134 | 136 | 138 | 140 |
| N | 1 | 0 | 1 | 0 | 1 | 1 | 3 | 0 | 3 | 3 | 4 | 7 | 9 | 4 | 12 |

There is no systematic account of the structural features (if any) shared by these extra closed shell isomers, and this puzzle is indicated by their naming as ‘sporadic’.⁵

Two obvious questions are:

Question 2.1

Is it possible to identify any infinite family among the sporadic fullerenes?

Question 2.2

Is there any sporadic fullerene that has adjacent pentagons?

These systematic observations can be represented on the HOMO-LUMO map. As explained in Ref. 1, the 45° line $\lambda_{\text{HOMO}} = \lambda_{\text{LUMO}}$ includes all the open-shells and separates ground from excited states. The triangular region with this line as hypotenuse contains the three types of closed shell: pseudo-closed shells above the horizontal axis, meta-closed shells to the left of the vertical axis, and properly closed shells in the square bounded by the horizontal and vertical axes (Figure 1). Vertical lines on the map link systems of equal HOMO eigenvalue (isohomal systems¹); horizontal lines link systems of equal LUMO eigenvalue (isolumal systems¹); lines of unit slope link systems of equal HOMO-LUMO gap (isodiastemal systems¹). Some researchers¹² use the weighted HOMO-LUMO separation, $n(\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}})$, as a rough measure of kinetic stability.

In terms of the HOMO-LUMO map, most fullerenes therefore appear in the triangular region between the open-shell line and the horizontal. Figure 2 shows the distribution of the 40 fullerene isomers of C_{40} and the 1812 fullerene isomers of C_{60} . All the C_{40} isomers, and all but one of the C_{60} isomers lie in the pseudo-closed region. These maps are examples of ‘horizontal’ samples of fullerenes, where all members of the set have equal vertex counts; a ‘vertical’ sample, of fullerenes of different orders that share icosahedral symmetry is shown in Figure 3. Icosahedral (I or I_h symmetric) fullerenes have $n = 20(i^2 + ij + j^2)$ vertices, with integer parameters $i \geq j$, $i > 0$, $j \geq 0$. In this set, therefore, either n is a multiple of 60, and the fullerene has a (leapfrog) properly closed shell, or division of n by 60 leaves remainder 20, and the fullerene has an open shell.¹³

HOMO and LUMO eigenvalues for icosahedrally symmetric fullerenes with values of n up to several thousand vertices have been tabulated,¹⁴ and Figure 3 shows the trajectories of the two icosahedral subsets as n runs through the allowed values 20, 60, 80, The open-shell C_{20} lies at the origin of the map. Other members of the open-shell series march in monotonically towards the origin along the map diagonal, starting from C_{80} , at (λ, λ) , where λ is the middle root of $x^3 + x^2 - 4x + 1 = 0$ (≈ 0.27389). The members of the closed shell series follow a curve in towards the origin from the C_{60} point. Icosahedral C_{60} has $\lambda_{\text{HOMO}} = (\sqrt{5} - 1)/2 = \phi^{-1} \approx 0.6180$;

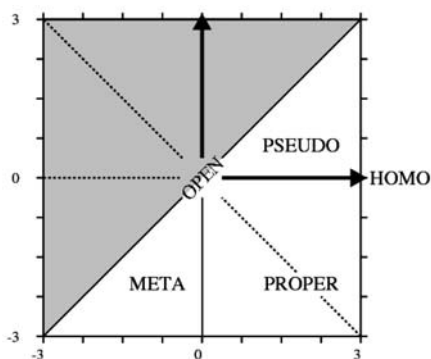


Figure 1: The HOMO-LUMO map separates ground from excited states (shaded area) and gives a geographical representation of the types of open and closed shell.

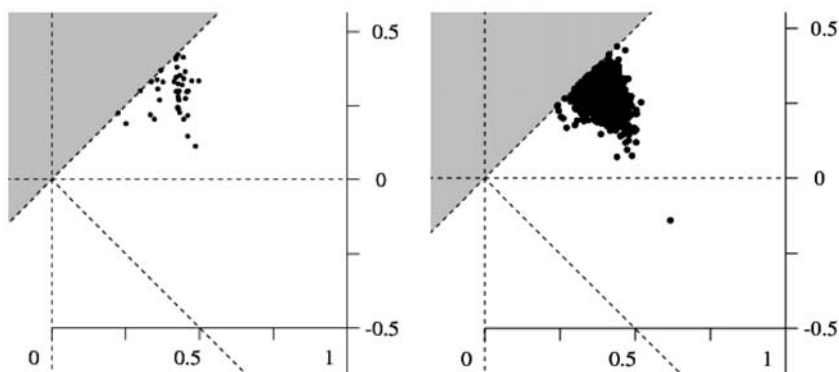


Figure 2: Fullerene HOMO-LUMO maps: The 40 fullerene isomers of C_{40} (left) and (right) the 1812 fullerene isomers of C_{60} . The single point in the properly closed-shell quadrant corresponds to the experimental structure of C_{60} .

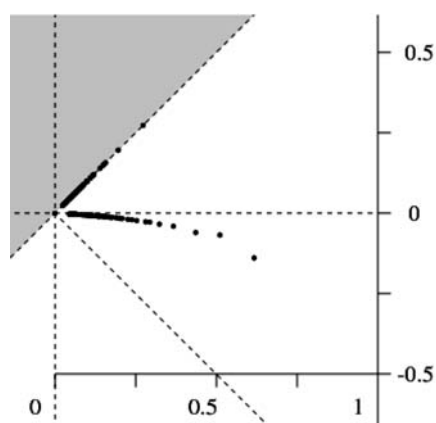


Figure 3: Fullerene HOMO-LUMO maps: Icosahedral fullerenes with from 20 to 37500 vertices. The eigenvalues are taken from a list that is extensive, although not complete at large n .¹⁴ The map shows the split into open and properly closed shells according to $n \bmod 60$, as described in the text.

$\lambda_{\text{LUMO}} = 1/4(3 + \sqrt{5} - (38 - 2\sqrt{5})^{1/2}) \approx -0.1386$, where ϕ is the golden ratio, leading to a HOMO-LUMO gap of $1/4(\sqrt{5} - 5 + (38 - 2\sqrt{5})^{1/2}) \approx 7.566$.

From extensive calculations on fullerene spectra (as reported in e.g., Refs. 5, 7, 14, 15), it appears that the point in the HOMO-LUMO map representing icosahedral C_{60} is extremal amongst all fullerenes. At the opposite end of the stability scale, C_{20} occupies the origin of the map, and extensive calculations have not revealed another fullerene with $\lambda_{\text{HOMO}} = \lambda_{\text{LUMO}} = 0$, although multiple zero eigenvalues do occur in the spectra of some other fullerenes.¹⁶

Some natural questions that arise are therefore:

Question 2.3

Is there a fullerene with $|\lambda_{\text{HOMO}}| > \phi^{-1}$?

Question 2.4

Is there a fullerene with $|\lambda_{\text{HOMO}} - \lambda_{\text{LUMO}}| > 1/4(\sqrt{5} - 5 + (38 - 2\sqrt{5})^{1/2})$?

Question 2.5

Is C_{20} the only fullerene with a properly open shell?

The isomer distributions for C_{40} , C_{60} and the icosahedral fullerenes (Figures 2 and 3) exhibit open and closed shells of properly and pseudo types in each case. Some meta-open shells have been found amongst large fullerenes of tetrahedral symmetry. All 21 recorded examples⁷ with $628 \leq n \leq 1000$ vertices lie very close to the origin on the HOMO-LUMO map. All have triply degenerate eigenvalues $\lambda_{\text{HOMO}} = \lambda_{n/2} = \lambda_{n/2+1} = \lambda_{n/2+2}$. So far, no meta-closed fullerenes have been identified, but no proof has been offered that they do not exist.

Question 2.6 *Is there a meta-closed fullerene?*

3. Closed-shell Fullerenes and HOMO-LUMO Maps

The three rules given earlier for properly closed shells lead to different geographical spreads in the maps. Fullerenes of the leapfrog class appear on the interior of the properly-closed region; carbon cylinder fullerenes all have $\lambda_{\text{LUMO}} = 0$ and hence lie on the horizontal line dividing pseudo and properly closed shells; the sporadic closed-shell fullerenes appear in a very thin just under the horizontal line (see Figure 4). As graphs that are 3-regular, all fullerenes have $|\lambda_{\text{HOMO}}| \leq \sqrt{3}$ and $|\lambda_{\text{LUMO}}| \leq \sqrt{3}$.¹ As noted above, eigenvalue calculations on fullerenes support the conjecture that these bounds can be further reduced to ϕ^{-1} for them.

This distribution seems to avoid the lower triangle of the properly-closed shell quadrant of the map, prompting the question:

Question 3.1

Are there fullerenes with properly closed shells and $|\lambda_{\text{LUMO}}| \geq |\lambda_{\text{HOMO}}|$?

The HOMO-LUMO map also gives some insight into the effect of iterating the leapfrog transformation of a fullerene. Figures 5 and 6 show the sequence of maps obtained by leapfrogging the C_{40} and C_{60} fullerene isomer

sets. Comparison with the maps shown in Figure 2 shows some clear trends. Most obviously, on leapfrogging, all the fullerenes move into the upper triangle of the properly closed-shell quadrant. On repeated leapfrogging, the distribution of the derived fullerenes moves closer to the origin, as both λ_{HOMO} and λ_{LUMO} are on average reduced in

magnitude. What is not obvious from the map is that the isomer with the largest HOMO eigenvalue in each successive leapfrog generation is the leapfrog of the isomer with largest HOMO eigenvalue from the previous generation. Thus, isomer 40:39 at 0.4865, 0.1134 on successive leapfrogging yields isomers of C_{120} , C_{360} and C_{1080} at 0.5207,

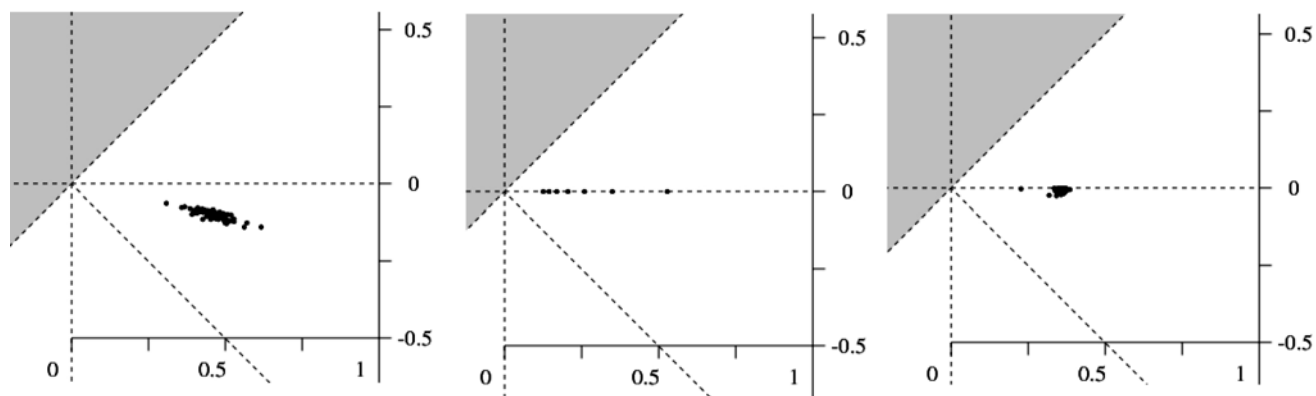


Figure 4: The three regions of the HOMO-LUMO map occupied by properly closed-shell fullerenes. From left to right: leapfrog fullerenes ($60 \leq n \leq 120$) occupy the upper triangle of the properly closed quadrant, carbon cylinders ($70 \leq n \leq 240$) lie on the horizontal ($\lambda_{\text{LUMO}} = 0$) boundary of this quadrant, and the sporadic closed shells ($112 \leq n \leq 140$) lie within the quadrant, and just below the horizontal.

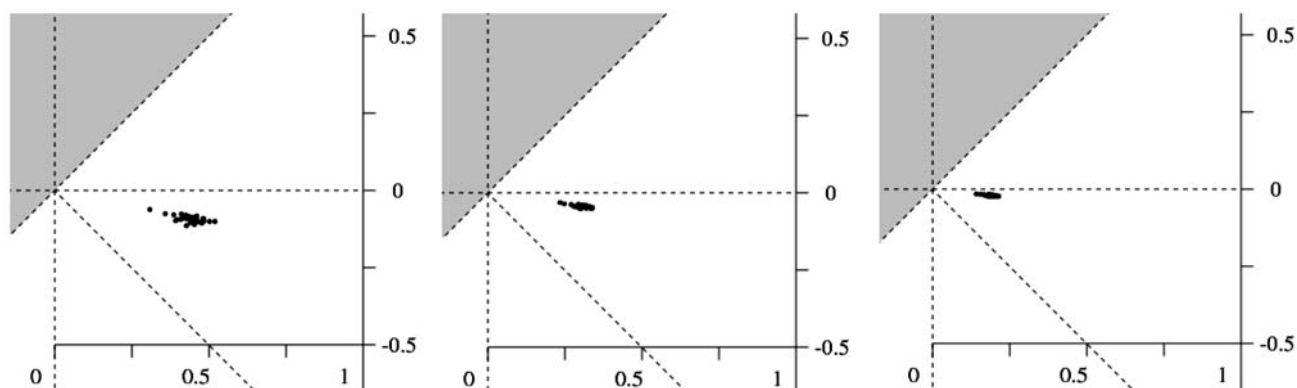


Figure 5: Leapfrog trajectories on the fullerene HOMO-LUMO map. The maps from left to right show the results of leapfrogging the 40 C_{40} fullerenes once, twice and three times, respectively.

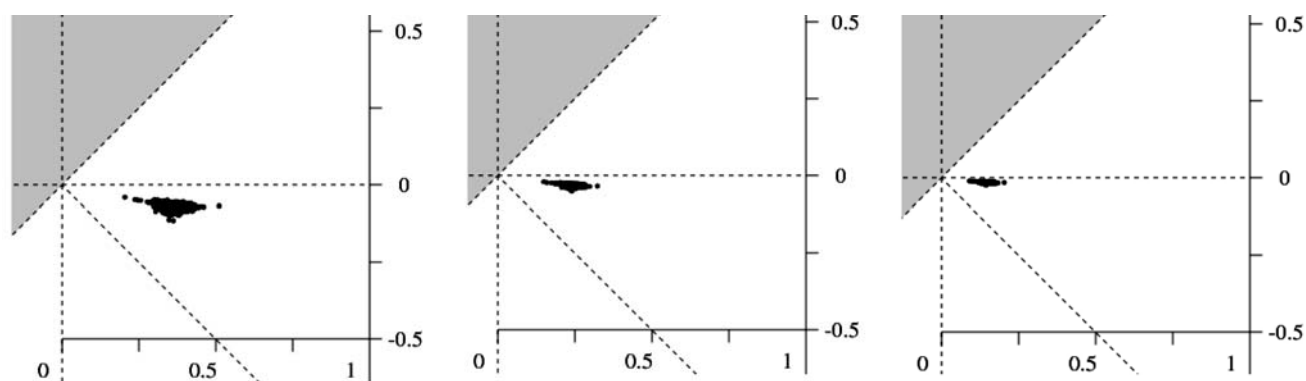


Figure 6: Leapfrog trajectories on the fullerene HOMO-LUMO map. The maps from left to right show the results of leapfrogging the 1812 C_{60} fullerenes once, twice and three times, respectively.

–0.0993, 0.3403, –0.0483, 0.2155, –0.0224, respectively; isomer 60:1812 at 0.6180, –0.1386 on successive leapfrogging yields isomers of C_{180} , C_{540} and C_{1620} at 0.5141, –0.0074, 0.3241, –0.0337, 0.2046, –0.0150, respectively. These particular samples are successively smaller subsets of the totality of leapfrog isomers, of isolated-pentagon isomers and of general fullerenes, but the trend suggests some questions:

Question 3.2

For values of n where a leapfrog isomer exists, is the isomer with maximum HOMO always a leapfrog?

Question 3.3

For values of n where a leapfrog isomer exists, is the isomer with maximum HOMO-LUMO gap always a leapfrog?

Question 3.4

Is the fullerene C_{3n} of maximum λ_{HOMO} the leapfrog of the fullerene C_n of maximum λ_{HOMO} ?

Question 3.5

Is the fullerene C_{3n} of maximum HOMO-LUMO gap the leapfrog of the fullerene C_n of maximum HOMO-LUMO gap?

4. Conclusion

Mapping HOMO and LUMO eigenvalues has helped to concentrate attention on some of the many open questions about fullerene eigenvalue spectra. A number of these questions could be combined into the more general problem of defining for a given class of graphs the convex hull of the points on the HOMO-LUMO map.

In this paper the focus of the discussion of HOMO-LUMO maps was placed entirely on fullerenes and their eigenvalue spectra. Possible further applications may be sought in several directions: (a) considering fullerene derivatives and decorating their HOMO-LUMO maps by determined values of physico-chemical properties, such as solubility,¹⁷ or (b) comparing HOMO-LUMO maps to theoretical measures of aromaticity.¹⁸

Note added in proof: With respect to Question 2.2: recent computational investigations have shown that there are in fact some (apparently rare) fullerenes with penta-

gon adjacencies that have properly closed shells. The unique smallest non-IPR fullerene with a properly closed shell has 120 vertices (P.W.F. and W. Myrvold, to be published).

5. References

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Povzetek

Zemljevidi HOMO-LUMO so uporabno orodje za klasifikacijo pi-elektronskih konfiguracij fulerenov in za določanje raziskovalnih problemov o njihovih sosednostnih spektrih.