

Matching spectra of fullerenes

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Abstract

Peculiarities in the distributions of roots of matching polynomials are pointed out. It was found that matching spectra of isomers with the same number of atoms show an exceptionally high degree of similarity. Individual values typically vary in the second or higher decimal places. Their average values drawn versus the size of the fullerene produce a clear pattern which indicates possible analytical form of the matching spectra of fullerenes.

1 Introduction

Matching polynomials of fullerenes are required for the evaluation of the resonance energy of fullerenes. Although the resonance energy is not a well defined physical quantity, it is successfully correlated with the stability of conjugated systems [1]. Several models have been developed for quantification of resonance energy, but only two remained in wide use: the conjugated circuit model [2] and the topological resonance energy model [3]. The results obtained from these two approaches are in qualitative agreement, and only recently more significant differences have been found, just in their application to fullerene-like systems [4].

If one disregards their obvious non-planarity, fullerenes are exemplary and almost ideal conjugated systems: each carbon atom participates in the common delocalized system. Their structure can be considered as a kind of graphite structure, minimally distorted in order to produce a finite (spherical) representation. After this comparison, fullerenes were anticipated to have fully delocalized π -electrons and electronic structure similar to graphite. However, it turned out that the curvature of their structure has a remarkable

effect, and that the extent of delocalization is far less than expected [5]. Accordingly, the interest for the computation of their resonance energy increased. The conjugated circuit model was the first to be systematically applied to fullerene isomers [6]. Due to the computational difficulties present in the evaluation of the matching polynomial, the topological resonance energy model has been, so far, applied only to fullerenes of smaller size [7] or to particular bigger isomers, such as C_{60} [8] or C_{70} [9]. Quite recently an efficient algorithm [10] for the calculation of matching polynomials has been developed and applied for massive computation of all fullerene isomers with up to 70 atoms. The results [11] showed some distinct and interesting properties of the topological resonance energy of fullerenes and of their matching polynomials. These properties will be further elaborated here.

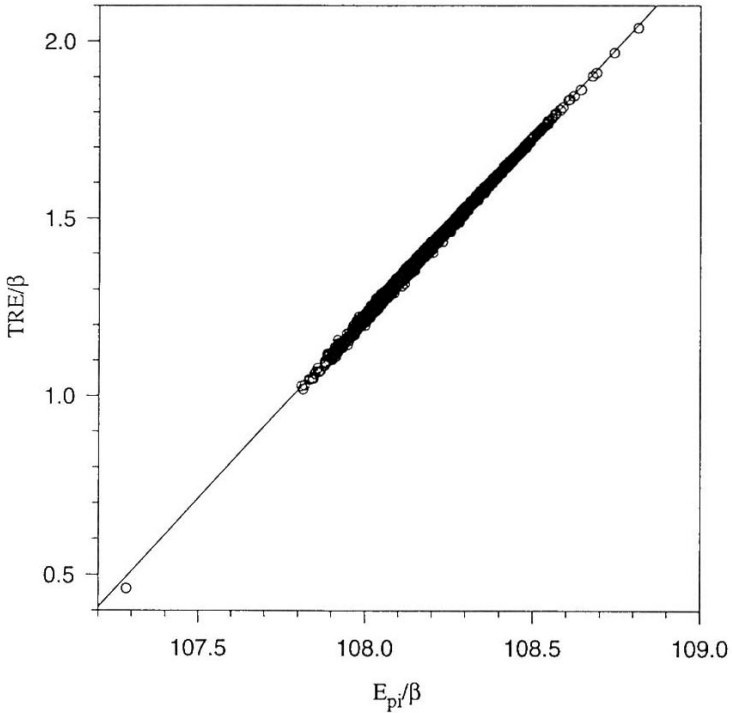


Figure 1: TRE values for 8149 isomers of C_{70} drawn versus E_r .

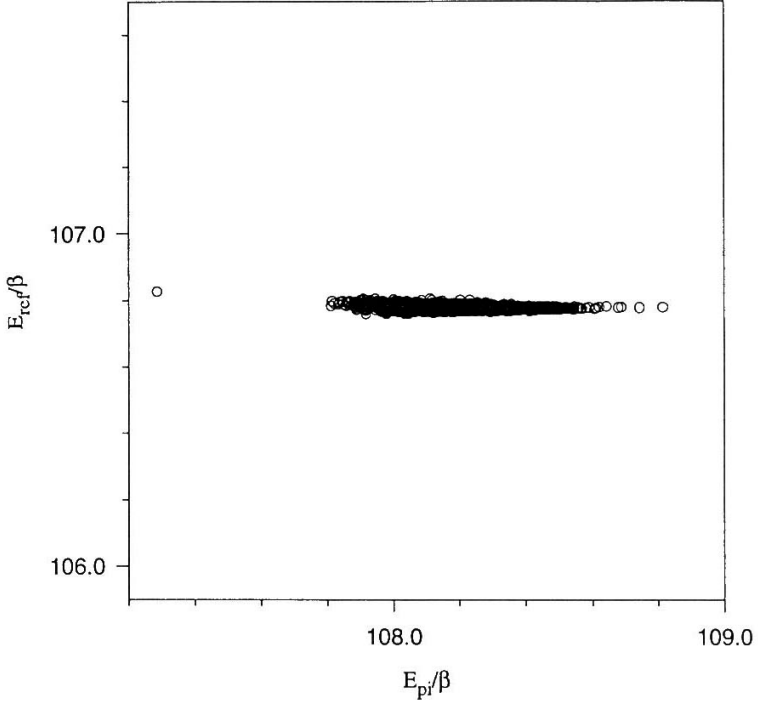


Figure 2: E_{ref} values for 8149 isomers of C_{70} drawn versus E_{π} .

2 Results

Recall first the definition of the matching polynomial, $\alpha(G)$:

$$\alpha(G) = \sum_{k=0}^{N/2} (-1)^k p(G, k) x^{N-2k}$$

where $p(G, k)$ stands for the number of choices of k pairwise non-incident edges in G . The properties of the matching polynomial are reviewed in [12]. It is used for evaluation of the topological resonance energy, TRE , according to the formula:

$$TRE = E_{\pi} - E_{ref}$$

where E_{π} stands for the π -electron energy evaluated within the framework of the Hückel model. Let $A(G)$ be an adjacency matrix of the graph G . The characteristic polynomial

of G , denoted by $\phi(G; \mathbf{x})$, is defined as:

$$\phi(G; \mathbf{x}) = \det[\mathbf{x}I - A(G)]$$

According to the Hückel model, the roots of the characteristic polynomial represent the π -orbital energies. Sum of orbital energies populated in the ground state yields E_π . The matching polynomial is used for the definition of the reference energy, E_{ref} , since its coefficients can be viewed as derived from those of the characteristic polynomial, by omitting the contributions of cyclic Sachs graphs [3]. In this way the matching polynomial is chosen to implicitly represent the reference acyclic structure. The roots of the matching polynomial are considered as π -orbital energies of the (hypothetical, not really existing) reference structure. E_{ref} is obtained by summing orbital energies populated in the ground state. As a straightforward consequence of the definition of matching polynomial, E_{ref} turns out to be equal to the sum of absolute values of its roots. The roots of the characteristic polynomial are identical to the eigenvalue spectrum of the adjacency matrix $A(G)$, shortly called the Hückel or characteristic spectrum. By analogy, the roots of the matching polynomial are shortly called the matching spectrum. The characteristic spectrum is real due to the Hermitian character of the adjacency matrix. An important finding for application of the matching polynomial in the above context is that the matching spectrum is also real [12].

The recently devised efficient algorithm for the computation of matching polynomials [10] has allowed evaluation of TRE for a number of fullerene isomers. Some earlier findings [4], which pointed out an unusually good linear correlation between TRE and E_π of fullerenes, have now been confirmed. An example can be seen in Fig. 1 where TRE values of all 8149 isomers of C_{70} are drawn versus E_π . A closer inspection reveals that this is due to the very small variations of E_{ref} of fullerenes possessing equal numbers of carbon atoms. In Fig. 2 are depicted the E_{ref} values of the same set of C_{70} isomers versus their E_{pi} values. Note that the scales on both axes are the same.

Our study showed that the E_{ref} values are more or less constant in the set of equally sized fullerene isomers, because their matching spectra possess a great similarity. That is, the roots of the matching polynomials obtained from different fullerene isomers (with the same number of atoms) are very similar. A degree of variations present in matching spectra can be seen in Fig. 3 where a cumulative distribution of matching spectra for C_{70} isomers is shown. Values of the individual roots are grouped into narrow and separate maxima. The width of maxima varies from $8.16 \cdot 10^{-4}$ (for higher root values) to $2.35 \cdot 10^{-2}$ (for lower root values). A comparison with the distribution obtained for characteristic spectra indicates how unusual is this feature of the matching spectra. In Figs. 4 and 5 are separately shown the cumulative distributions for the negative and positive roots of characteristic polynomials of the same set of C_{70} isomers. In the spectrum of each isomer the eigenvalues are ordered by their magnitude, and those with the same order in all considered isomers are grouped together. Bell-shaped curves in Figs. 4 and 5 are distributions obtained for eigenvalues of the same orders. Note the overlap of distributions pertaining to eigenvalues of different orders, and a large difference with respect to the distribution of the matching spectra.

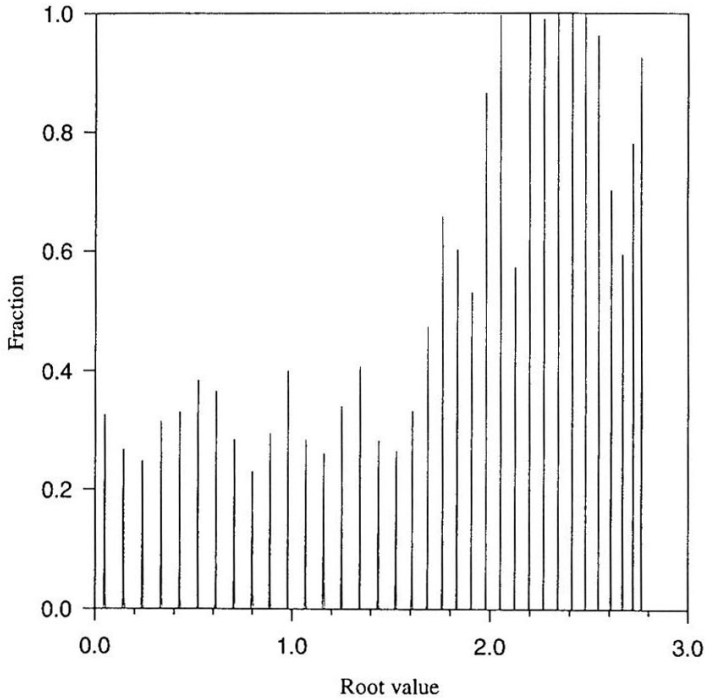


Figure 3: Cumulative distribution of matching spectra obtained for C_{70} isomers.

At this moment we cannot offer some quantitative explanation for the above findings. It is instructive to recall that the matching polynomial is introduced [3] with the aim to suppress an effect of the cycles in the molecular structure. The chief difference between fullerene structures of the same size is in the way their rings (six- and twelve five-membered) are arranged. If the effects of rings are somehow disregarded, then one could expect that different isomers will show even greater degree of similarity. The similarity shown by their matching spectra (and, consequently, matching polynomials too) is in good agreement with this expectation. Thus, one could extend this qualitative explanation to a conclusion that the relative invariability of matching polynomials of fullerenes supports their use for the definition of the reference structure.

While the grouping of the roots of matching polynomials in the cumulative distribution shown in Fig. 3 is self-evident, it can be a matter of dispute when characteristic poly-

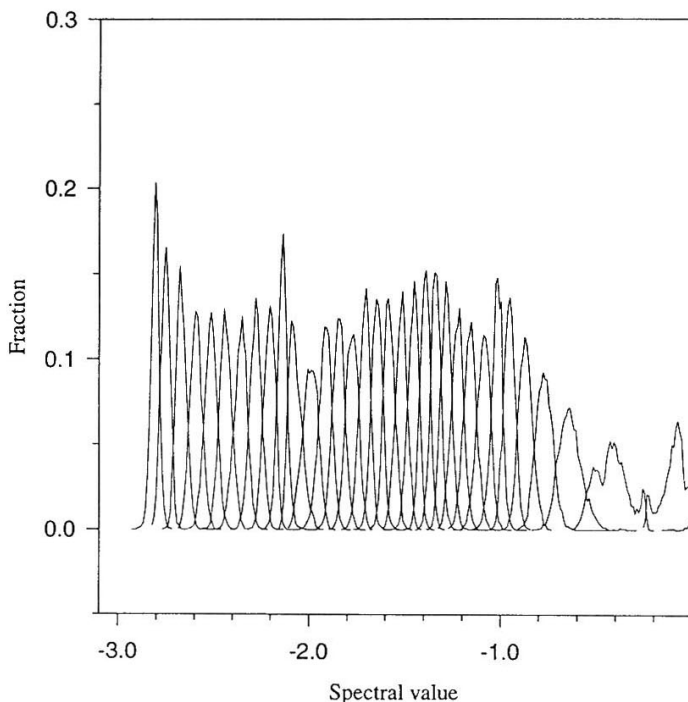


Figure 4: Cumulative distribution of negative part of characteristic spectra obtained for C_{70} isomers.

mials are concerned. One might doubt whether considering the characteristic spectra as shown in Figs. 4 and 5 is appropriate at all. For example, instead of grouping roots of the same order, one might draw cumulative distributions for all roots. Nevertheless, it seems that there is an additional sense in the grouping of the characteristic roots. Figs. 6 and 7 show average values for each group drawn versus the size of the fullerene isomers. Both figures indicate the presence of a distinct pattern, which is especially regular for matching spectra. The regularity of the characteristic spectra, shown in Fig. 7, is more complex and more pronounced for fullerenes possessing over 40 atoms, for which the number of isomers is higher and for which the average values can be expected to be more significant. Interpretation of these findings yet awaits to be done.

As a final remark we mention that so far not a single case of matching spectrum with

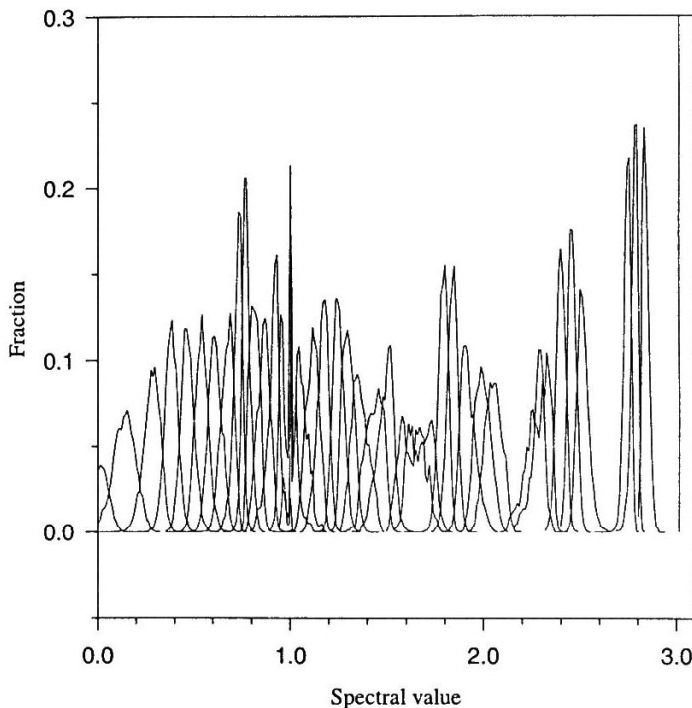


Figure 5: Cumulative distribution of positive part of characteristic spectra obtained for C_{70} isomers.

degenerate roots has been encountered for fullerenes studied (with at most 70 carbon atoms). Godsil proved [13] that the matching polynomial of a graph with a self-avoiding path extending through k edges possesses at least $k+1$ distinct roots. Consequently, all roots of the matching polynomial of a graph possessing a Hamiltonian path are distinct. Thus the observed absence of degenerate roots is in full agreement with the finding that all isomers in the studied set possess a Hamiltonian cycle [14] (which, of course, implies that they also possess Hamiltonian paths).

3 Conclusions

Matching spectra of fullerene isomers of the same size exhibit a great deal of similar-

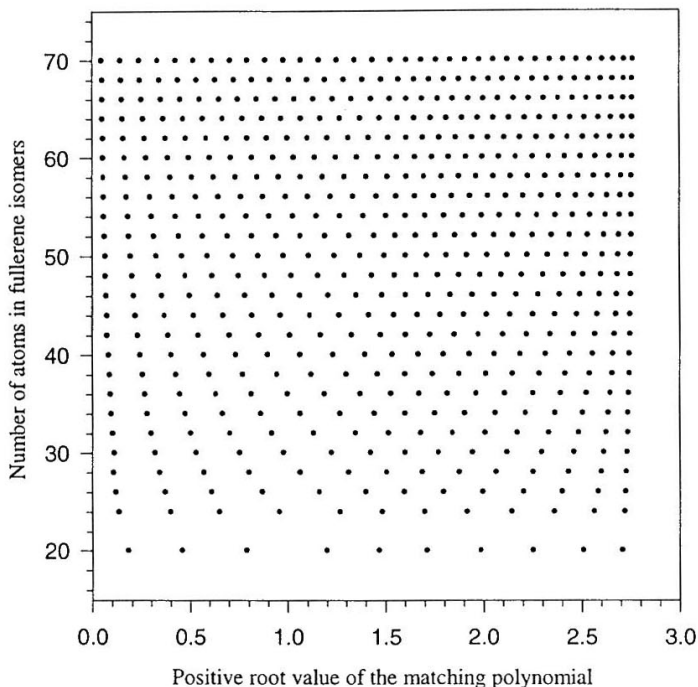


Figure 6: Average matching spectra obtained for fullerenes of various sizes.

ity. Typically, root values vary only in the second or higher decimal places. Cumulative distributions obtained for all isomers of the same size show that the roots of the matching polynomials are grouped into narrow and discrete intervals. The analogous superposition of distributions of the eigenvalues of the same order in the characteristic spectra shows a quite different picture, with extended and overlapping intervals. Clearly, matching polynomials of fullerenes are similar to an exceptionally high degree, which can be understood as a consequence of the similarity of the implicitly conceived underlying acyclic structures. It was clearly demonstrated for fullerene isomers of C_{70} , but the same features are found to be present for all classes of smaller fullerenes.

The average values of the roots of the characteristic and matching polynomials, drawn versus the fullerene size, show an unexpected regularity which is particularly pronounced for roots of the matching polynomials. The emerging pattern indicates a possible existence

of some analytical form of the matching spectra of fullerenes.

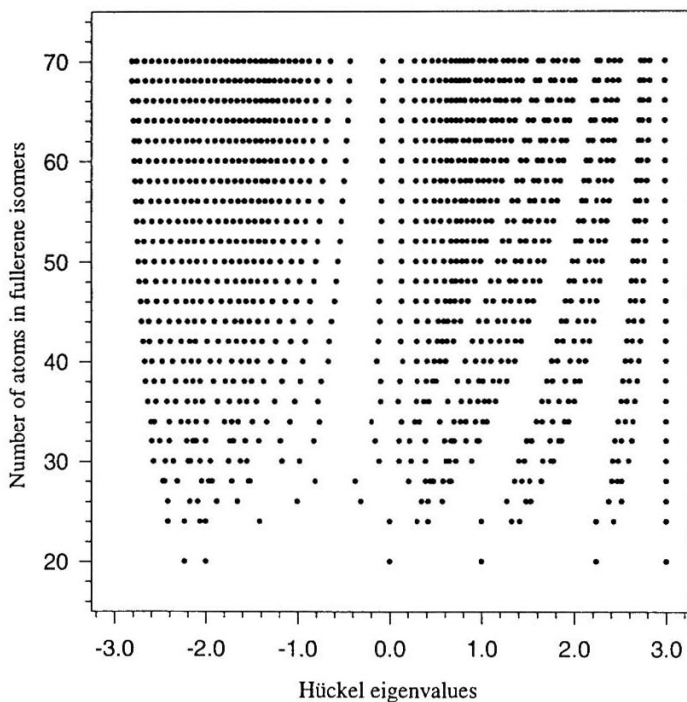


Figure 7: Average characteristic spectra obtained for fullerenes of various sizes.

4 Acknowledgements

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