The largest eigenvalues of adjacency and Laplacian matrices, and ionization potentials of alkanes

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Received 11 February 2002

If \( G \) is a molecular graph and \( A(G) \) its adjacency matrix, then the Laplacian matrix is defined as \( L(G) = D(G) - A(G) \) where \( D(G) \) is the diagonal matrix of vertex degrees. We establish a relation between the largest eigenvalues of \( A(G) \) and \( L(G) \) in case of the molecular graphs of alkanes. This relation is linear, but differs for alkanes with and without a quaternary carbon atom, revealing the main features of the structure-dependence of their (first) ionization potential. An analogous, yet more general, relation holds for all trees.

Let \( G \) be a molecular graph possessing \( n \) vertices. If these vertices are labeled by \( v_1, v_2, \ldots, v_n \), then the adjacency matrix of \( G \), denoted by \( A(G) = ||A(G)|| \), is defined as:

\[
A(G)_{ij} = \begin{cases} 
1, & \text{if vertices } v_i \text{ and } v_j \text{ are adjacent} \\
0, & \text{otherwise}
\end{cases}
\]

The characteristic polynomial of \( G \) is:

\[
\phi(G, \lambda) = \det(\lambda I - A)
\]

where \( I \) stands for the unit matrix of order \( n \). The roots \( \lambda_1, \lambda_2, \ldots, \lambda_n \) of \( \phi(G, \lambda) \) are the eigenvalues of the graph \( G \) and form its spectrum. The largest eigenvalue is denoted by \( \lambda_1 \).

The degree of a vertex \( v_i \) is the number of its first neighbours and is denoted by \( d_i \). In a molecular graph no vertex degree is greater than four.

The Laplacian matrix of \( G \) is defined as:

\[
L(G) = D(G) - A(G)
\]

where \( D(G) \) is the diagonal matrix of vertex degrees.

The eigenvalues of \( L(G) \), denoted by \( \mu_1, \mu_2, \ldots, \mu_n \), are called the Laplacian eigenvalues and form the Laplacian spectrum of \( G \). The largest Laplacian eigenvalue is \( \mu_1 \) while the smallest one, \( \mu_n \), is equal to zero.

A tree is a connected acyclic graph. In this work we are concerned with molecular graphs of alkanes, the so-called chemical trees. A chemical tree is a tree in which the maximal vertex degree is less than or equal to 4. There are two kinds of chemical trees – vertex-filled (plerograms), in which vertices stand for both carbon and hydrogen atoms, and vertex-depleted (kenograms) in which vertices represent only carbon atoms, see Fig. 1.

The elucidation of the dependence of various chemical and physical properties of substances on molecular structure can be considered as one of the main goals of theoretical chemistry. One direction in these structure-property studies employs quantities based on and calculated from the molecular graph. Such graph invariants are often called topological indices.

Some topological indices are related to graph eigenvalues. First of all, the largest eigenvalue \( \lambda_1 \) was, long time ago, put forward as a measure of molecular branching. Recently Randić et al. used the largest eigenvalues of several graph-based matrices, among which was also \( \lambda_1 \), for describing the shape and folding of DNA molecules; they applied \( \lambda_1 \) also in the study of physicochemical properties of alkanes. For another direction of research, related to \( \lambda_1 \), see the paper.

Another important topological index that can be calculated from the spectrum of a chemical tree is the Hosoya index, which obeys the relation:

\[
Z = \sqrt[n]{\prod_{i=1}^{n}(1 + \lambda_i^2)}
\]

We mention in passing that the eigenvalues of the molecular graphs of unsaturated compounds play an important role also in the Hückel molecular orbital theory.
Figs. 1—Molecular graphs of 3-methylpentane (kenogram Ke1 and plerogram Pl1) and 2,2-dimethylpentane (kenogram Ke2 and plerogram Pl2), and the respective line graphs of the plerograms, A(P/1) and A(P/2). The first alkane does not, whereas the second does possess a quaternary carbon atom. Note that n, is the number of carbon atoms, then the kenogram possesses n vertices whereas the plerogram 3n+2 vertices. Therefore, the computation of the eigenvalues is much more difficult for plerograms than for kenograms.

The Laplacian spectrum found several applications in the theory of saturated hydrocarbons. In the case of trees, a much studied molecular structure-descriptor, the Wiener index 

\[ W = n \sum_{i=1}^{n} \frac{1}{\mu_i} \]

In 1977, Heilbronner\(^\text{16-18}\) proposed a quantum-chemical model of the photoelectron spectra of saturated hydrocarbons. Within this model the ionization potentials of the C₂s electrons are in a simple linear relation with the eigenvalues of the line graph of the respective plerogram. (Details on line graphs can be found in\(^\text{10,20}\), see also Fig. 1.) On the other hand, if G is an n-vertex tree, then the eigenvalues of its line graph \(\lambda(G)\) are related to the Laplacian eigenvalues of G as\(^\text{31}\):

\[ \lambda_i(A(G)) = \mu_i(G) - 2, \quad i=1,2,\ldots,n-1 \]  

Equation (1) implies that from the largest Laplacian eigenvalue of a plerogram one can infer on the first C₂s ionization potential, i.e., on the position of the lowest-lying high-energy band in the photoelectron spectrum of an alkane; for more details see\(^\text{22,23}\).

Instead of studying the \(\mu_i\)-values of the plerograms (which is somewhat difficult because of the large number of vertices, cf. Fig. 1) we can consider the \(\mu_i\)-values of the kenograms. Namely, between \(\mu_i(Pl)\) and \(\mu_i(Ke)\) there exist a reasonably good linear correlation. An example of such a correlation is shown in Fig. 2.

We, thus, see that the largest eigenvalues of both the adjacency and the Laplacian matrix of chemical trees are encountered in various theoretical approaches to saturated hydrocarbons. It is, therefore, of some interest to examine their mutual relation. The results obtained along these lines are outlined in the subsequent section. These shed some light on the origin and structure-dependence of the (first) ionization potentials of alkanes.

A relation between \(\lambda_1\) and \(\mu_1\)

In order to establish the relation between \(\lambda_1\) and \(\mu_1\) we examined sets of isomeric alkanes and plotted their \(\mu_i\)-values versus the \(\lambda_i\)-values. In Fig. 3 a characteristic example is depicted.

In the case of alkane isomers, the relation between \(\lambda_1\) and \(\mu_1\) is linear but the data-points are grouped into two clearly separated clusters. There is a single "outlier", corresponding to the normal (unbranched) alkane. This kind of regularity was observed for isomeric alkanes with \(n = 6, 7, 8, 9, 11, 12, 13, 14\) and \(15\) carbon atoms.
We further found that all data-points belonging to the same group correspond to chemical trees with same maximal vertex degrees, \( d_{\text{max}} \). Because the value of the maximal vertex degree in a molecular graph cannot exceed four, we have only three possibilities:

(i) the maximal vertex degree is equal to 2.
(ii) the maximal vertex degree is equal to 3.
(iii) the maximal vertex degree is equal to 4.

(Exceptionally, the molecular graph of ethane has \( d_{\text{max}} = 1 \).

For alkanes with a fixed number of carbon atoms, only a single chemical tree has \( d_{\text{max}} = 2 \) – the molecular graph of the normal alkane, the only unbranched chemical tree, the "outlier" in Fig. 3. All other (branched) chemical trees are then divided into two groups: those with \( d_{\text{max}} = 3 \) and those with \( d_{\text{max}} = 4 \). Evidently, if \( d_{\text{max}} = 3 \), then the respective alkane possesses tertiary, but no quaternary carbon atoms. If \( d_{\text{max}} = 4 \), then at least one quaternary carbon atom is present in the respective alkane.

The regularity described above is not restricted to chemical trees. We found that in the case of all \( n \)-vertex trees an analogous relation between \( \lambda \) and \( \mu \) exists. Here, however, there are more groups of data-points because in the case of trees the maximal vertex degree assumes values between 2 and \( n-1 \). This regularity is illustrated in Fig. 4 for the 10-vertex trees; analogous results were observed for all \( n \) from 6 to 15.

**Discussion**

In Table 1 are given the details on the linear correlation between \( \lambda \) and \( \mu \) in the case all alkanes with \( 6 \leq n \leq 15 \) carbon atoms (except the normal alkanes, for which \( d_{\text{max}} = 2 \)). These results corroborate the conclusion that the relation between \( \lambda \) and \( \mu \) is (as a reasonably good approximation) linear, but holds only within groups of isomers with the same value of \( d_{\text{max}} \). This, in turn, means that – as far as the structure-dependency of \( \mu \) is concerned – one has to distinguish between two groups of alkanes; those with quaternary carbon atoms \( \left( d_{\text{max}} = 4 \right) \) and those with tertiary, but without quaternary carbon atoms \( \left( d_{\text{max}} = 3 \right) \). Within each group, \( \mu \) is a (linearly) increasing function of \( \lambda \), implying that it depends on the branching of the carbon-atom skeleton, and that it increases with the increasing extent of branching.

At this moment we are not able to offer a rigorous mathematical demonstration of the fact that the nature of the correlation between \( \lambda \) and \( \mu \) significantly depends on \( d_{\text{max}} \), and that this regularity is by no means restricted to chemical trees. On the other hand, bearing in mind Heilbronner's theory\(^{16,18}\), our results clearly indicate that the first ionization (of \( \text{C}_n^2 \) electrons) occurs at a quaternary carbon atom (if such an atom is present in the molecule), and at a tertiary carbon atom otherwise. If neither quaternary nor tertiary carbon atoms are present (which is the case only with normal alkanes), then the ionization takes place at a secondary carbon atom. The energy required to ionize a quaternary carbon atom is significantly lower than the ionization energy of a tertiary carbon atom, which again is much lower than
the ionization energy of a secondary carbon atom. This feature causes the clustering of our data-points into two groups and an "outlier".

Branching of the carbon-atom skeleton increases the ease of ionization and thus decreases the ionization potential. It turns out that the branching-dependence of the (first) ionization potential is well, reproduced by the largest eigenvalue of the adjacency matrix, and that its dependence on $\lambda_1$ is nearly linear.