

Examination of the Statistical Method in the Conjugated Circuit Theory

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Summary. The recently proposed statistical method for the calculation of resonance energies in the conjugated circuit theory is tested on the example of polyacenes. It is found that for the estimation of the resonance energy with a 10% average error, the method requires a sample consisting of about 20 (randomly chosen) Kekulé structures. Further increase of the sample size gives no significant gain in the accuracy of the method.

Keywords. Conjugated circuits; Conjugated circuit theory; Kekulé structures; Resonance energy.

Überprüfung der statistischen Methode in der „Konjugierten-Ring-Theorie“

Zusammenfassung. Die unlängst vorgeschlagene statistische Methode in der „Konjugierten-Ring-Theorie“ (conjugated circuit theory) wird am Beispiel der Polyacene getestet. Es wurde festgestellt, daß für die Abschätzung der Resonanzenergien bei einem mittleren Fehler von 10% für diese Methode ungefähr 20 (willkürlich gewählte) Kekulé-Strukturen nötig sind. Weitere Erhöhung dieser Anzahl bringt keine signifikante Verbesserung der Genauigkeit der Methode.

Introduction

The conjugated circuit theory [1–4] is an approach proposed for the qualitative and semiquantitative description of the π -electron properties of conjugated molecules, first of all their aromaticity and resonance energy. The application of the theory requires the recognition and enumeration of linearly independent conjugated circuits, separately in each Kekulé structure of the conjugated system examined. For large polycyclic molecules, where hundreds and thousands of Kekulé structures occur [5], such a procedure becomes extraordinarily tedious and error prone. This drawback of the theory has been conceived several years ago [6], but a feasible solution could not be found. Recently [7] the use of a statistical, Monte-Carlo-type approach was put forward.

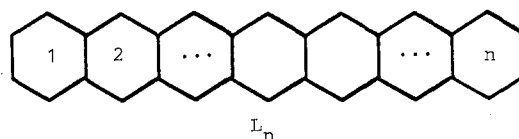
According to [7], instead of analysing the conjugated circuits in all Kekulé structures, only a limited number of them are examined. These latter Kekulé structures are to be selected uniformly by random and then they will provide a representative sample. (A random choice of elements of a set is said to be uniform if each element of the set has equal probability to be selected.) The results of the counting of independent conjugated circuits in this sample are expected to give a

realistic picture of the entire conjugation pattern of the molecule considered, and thus to enable a reliable estimation of its resonance energy and related quantities.

The aim of the present paper is to contribute towards a better understanding of the range and limitations of this statistical method.

Method

We have decided to test the statistical approach developed in [7] on the example of the linear polyacene L_n . The reasons for this are following.



(i) The numbers of conjugated circuits (contained in all Kekulé structures) of L_n are well known [4]. L_n contains $2(n - k)$ circuits of size $4k + 2$, $k = 1, 2, \dots, n$. In addition to this, the number of Kekulé structures of L_n is $n + 1$.

(ii) All conjugated circuits in each of the Kekulé structures of L_n are linearly independent. Therefore we do not encounter the difficult task of recognizing linear dependence between conjugated circuits.

(iii) It is very easy to construct a Kekulé structure of L_n uniformly by random. The conjugated circuits contained in this Kekulé structure are readily determined.

This enables one to construct the Kekulé structures and determine their conjugated circuits by means of a simple computer routine and the results reported in the present paper are based on the examination of more than ten million of randomly selected Kekulé structures. (In Ref. [7] the total number of Kekulé structures constructed and investigated was only a few hundred.)

Our method for the construction of a random Kekulé structure is based on the observation [8] that in each Kekulé structure of L_n exactly one double bond is vertical. When a vertical double bond is selected, all other double bonds are fixed and thus the entire Kekulé structure is determined. If one labels the vertical edges of L_n by $0, 1, \dots, n$ (say, by going from left to right), then the (random) selection of a Kekulé structure of L_n is equivalent to the (random) choice of an element from the set $\{0, 1, \dots, n\}$. This latter procedure is easy to do in a uniform manner. If r is a uniformly generated random number from the interval $(0, 1)$ and $[x]$ denotes the integer part of x , then $i = [r(n + 1)]$ is an element of $\{0, 1, \dots, n\}$ chosen uniformly by random. On the other hand, i corresponds to a Kekulé structure of L_n in which the vertical double bond is at the position i . This Kekulé structure is thus selected uniformly by random.

Further, the Kekulé structure of L_n having the vertical double bond in position i possesses conjugated circuits of size $6, 10, \dots, 4i + 2$ (provided $i \neq 0$) and additional conjugated circuits of size $6, 10, \dots, 4(n - i) + 2$ (provided $i \neq n$).

In Fig. 1 is depicted a Kekulé structure of L_7 with $i = 3$. It contains conjugated circuits of size 6, 10, 14, and 18 which are also presented in Fig. 1.

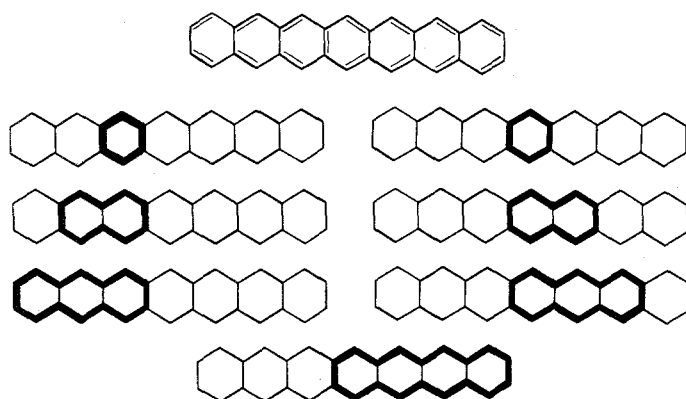


Fig. 1. The Kekulé structure of L_7 having the vertical double bond in position 3. It contains two conjugated circuits of size 6, 10, and 14 and an additional circuit of size 18

Results and Discussion

The numbers of conjugated circuits of various sizes in the Kekulé structures of L_n were estimated from a randomly chosen sample of Kekulé structures. The number of Kekulé structures in the sample (= size of the sample) is denoted by S . For a given value of S , the selection of the sample was repeated 1 000 times and the difference between the estimated and exact values of the circuit counts (= error) calculated. In Table 1 the average values of these errors are presented for the case of L_{10} .

From Table 1 is seen that the average errors decrease with increasing S . This decrease is rapid until S reaches the value 10, but after that becomes very slow.

In the commonly used variant [1-4] of the conjugated circuit theory the resonance energy of benzenoid hydrocarbons is calculated by means of the formula

$$RE = (\rho_1 R_1 + \rho_2 R_2 + \rho_3 R_3 + \rho_4 R_4)/K$$

Table 1. Average errors (in %) of the estimated numbers of conjugated circuits of L_{10} as a function of S

Circuit size	Sample size										
	1	2	3	5	10	20	30	50	100	200	300
6	16	13	11	7.7	5.3	3.9	3.2	2.3	1.7	1.2	1.0
10	28	18	14	11	7.6	5.4	4.3	3.3	2.3	1.6	1.4
14	34	19	17	12	8.7	6.3	5.1	3.9	2.7	1.9	1.6
18	30	23	17	13	8.8	6.3	5.1	3.8	2.8	1.9	1.6
22	15	14	12	11	6.5	4.5	3.9	2.9	2.1	1.5	1.2
26	18	17	15	13	7.7	5.5	4.6	3.5	2.6	1.8	1.5
30	53	41	30	23	15	11	8.8	6.7	4.9	3.4	2.8
34	91	52	46	32	23	17	13	10	7.4	5.2	4.3
38	128	81	61	47	34	24	19	15	11	7.3	6.1
42	165	133	108	77	53	39	32	23	17	12	9.9

Table 2. Average error (in %) of the estimated resonance energy of L_{10} as a function of S ; note that $RE(L_{10}) = 13.44$ eV

S	Error	S	Error
1	35	30	6.3
2	26	50	4.7
3	22	100	3.4
5	16	200	2.4
10	11	300	2.0
20	7.8		

where ρ_k , $k = 1, 2, 3, 4$ are the numbers of independent conjugated circuits of size $4k + 2$, K is the number of Kekulé structures and R_k , $k = 1, 2, 3, 4$ are semi-empirical parameters. Their values are [1-4]: $R_1 = 0.869$ eV, $R_2 = 0.246$ eV, $R_3 = 0.100$ eV, $R_4 = 0.041$ eV.

In Table 2 are given the average errors when the resonance energy of L_{10} is calculated using the statistical method.

We note in passing that the value 0.041 eV for R_4 is a result of an apparent computational error made in Ref. [1]. The correct value of R_4 is 0.140 eV. Curiously, nobody seems to have checked the (otherwise quite easy) calculations from Refs. [1, 2] and as a consequence of this, the erroneous value for R_4 was systematically (and successfully!?) used in the literature. The resonance energies in the present paper are also computed with the usual choice 0.041 eV for R_4 .

Calculations of the above described type have been performed for several other linear polyacenes L_n . The results obtained are closely similar to those reported above for L_{10} .

With the plausible assumption that the basic features of the results obtained for L_n are characteristic to other polycyclic conjugated molecules as well (or at least to benzenoid hydrocarbons), we arrive at our final conclusions.

First, if a 10% error in the calculation of resonance energy can be tolerated, then the statistical method in the theory of conjugated circuits gives satisfactory results. In that case a sample of about 20 randomly chosen Kekulé structures will suffice. This makes the calculation of the resonance energy feasible even in the case of very large conjugated systems.

Second, the increase of the sample size over 20 gives no significant improvement in the accuracy and cannot be recommended. As a matter of fact, a tenfold increase of S results in the lowering of the average error of RE by a factor of about three. Even with extremely large samples, the error of the estimated RE remains well above 1%. Therefore the use of large samples (say, S greater than 30) is inexpedient and unjustified. If an accuracy better than 10% is desired, then the resonance energies should not be calculated by means of the statistical method.

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