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Statisco–Mechanical Aspect of the Hosoya Index

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Statisco–Mechanical Aspect of the Hosoya Index[#]

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Abstract

By using the partition function of a graph new topological indices, the bond index, B , and the connective index, C , are defined for analyzing the statisco-mechanical aspect of the Hosoya index, Z (here denoted by H). By comparing these three indices, B , C , and H for small graphs representing the carbon atom skeletons of hydrocarbon molecules, the physical meaning of H was found to be clarified by C .

Keywords. Hosoya index; connective index; partition function; statisco-mechanical theory; topological index; structural descriptor; molecular graph.

1 INTRODUCTION

The Hosoya index H was proposed three decades ago for a connected graph G representing the carbon atom skeleton of a saturated hydrocarbon molecule [1] (in the original paper [1] the notation Z was used instead of H). Empirical relations were proposed and discussed for the boiling points of saturated hydrocarbons and the Hosoya index [2]. The absolute entropy of acyclic saturated hydrocarbons was found to be well correlated linearly with the logarithm of H of the graph representing the carbon atom skeleton of hydrocarbons. The physical meaning of these relations was clarified by analyzing H and the rotational partition function [3]. It has been interpreted that H represents the dynamical features of the topological properties of these molecules [4–5]. Some other simple topological indices were derived and discussed by the author and colleagues [6–8]. The Hosoya index was also applied to π -electronic systems and some interesting results were obtained [9–11]. Thus, graph-theoretical analyses are found to be useful for explaining the topological features of the electronic states of molecules and lattices. For example, the number of perfect matchings for some lattices is a useful quantity in the theoretical treatment of adsorption of diatomic molecules on metallic surfaces (dimer statistics), nearest-neighbor interaction on the lattice points in anti-ferromagnetic metals (Ising model), and stability of aromatic hydrocarbon

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molecules (Kekulé structures counting).

In the case of dimer statistics, cylindrical and 3–dimensional lattice models were studied by the author and colleagues by use of graph theory [12–16]. In the present note the thermodynamic states of hydrocarbons themselves are not treated but the graph–theoretical aspects of the electronic states of the cyclic and acyclic molecules are discussed. In section 2 a partition function is defined on the assumption of Ising model for the graph G with which the electronic system of a hydrocarbon is expressed. In section 3 the Hosoya index H and the connective index C are defined from the partition function of a graph G [17]. Then the values of the connective index are calculated and compared with those of H . The aim of the present note is not to reveal the characteristics of the connective index itself but to analyze the nature of H in terms of the connective index from the viewpoint of statistical mechanics. A property of H and C is discussed from the viewpoint of statistical mechanics in section 4.

2 APPLICATION OF THE PARTITION FUNCTION

Usually a partition function is defined for a system composed of a large number of particles. However, in the present note it is applied to systems with a smaller number of electrons (say, one hundred electrons at most). Consider a graph G of the carbon atom skeleton of an unsaturated hydrocarbon from the viewpoint of the Ising model. When we want to calculate the partition function of a system of a saturated hydrocarbon we need to treat a graph describing, for example, all the 8 valence electrons surrounding a carbon atom nucleus. This makes the calculation of the partition function very complicated even for a small saturated hydrocarbon molecule. Therefore, in the present note we treat saturated hydrocarbons only mathematically. Namely, we suppose a hydrocarbon molecule is an ensemble composed of carbon atoms but not of electrons and nuclei. This means that in the case of saturated hydrocarbons the topological indices have not an explicit but indirect partition–functional meaning in the present note. $Z(N, T, h = 0)$ is a partition function of the system, where N , T and h are the number of vertices, the absolute temperature, and the magnetic field respectively [17]. The partition function Z is defined as follows:

$$Z(N, T, h = 0) = \sum_{\{s\}} \prod_{\langle ij \rangle} \exp(Js_i s_j), \quad (2.1)$$

where $J = E/kT$. Notations s_i and s_j stand for spins. E and k are the exchange energy and Boltzmann constant respectively [17]. The following mathematical formula is known:

$$\exp(As) = \cosh A + s \sinh A = \cosh A (1 + s \tanh A) \quad (2.2)$$

where $s = +1$ or -1 . From Eqs. (2.1) and (2.2) the next equation is obtained:

$$Z = (\cosh J)^P \sum_{\{s\}} \prod_{\langle ij \rangle} (1 + s_i s_j \nu) \quad (2.3)$$

where $v = \tanh J$, and p is the total number of nearest neighbor couples of spins. The following function $V(s)$ is defined for the later use:

$$V(s) = \prod_{\langle ij \rangle} (1 + v s_i s_j), \quad (2.4)$$

where we assume that s_i or s_j is $+1$ or -1 when we calculate the partition function itself because we assume the Ising model. However, as long as we are concerned with topological indices we assume s_i or s_j is always $+1$ because we treat the Hosoya index (see section 3). Examples of calculating partition functions are shown below.

In the case of graph I (π -electron system of butadiene, see Figure 1) $p = 3$. Then we have:

$$Z(N=4) / (\cosh J)^3 = \sum_{s_1=-1}^{s_1=+1} \sum_{s_2=-1}^{s_2=+1} \sum_{s_3=-1}^{s_3=+1} \sum_{s_4=-1}^{s_4=+1} V(s) \quad (2.5)$$

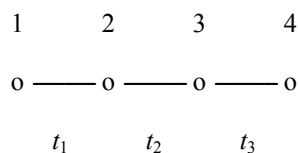


Figure 1. Graph I.

where $V(s)$ is expressed for the graph I as follows:

$$\begin{aligned} V(s) &= (1 + v s_1 s_2) (1 + v s_2 s_3) (1 + v s_3 s_4) = (1 + v t_1) (1 + v t_2) (1 + v t_3) \\ &= 1 + v (t_1 + t_2 + t_3) + v^2 (t_1 t_2 + t_1 t_3 + t_2 t_3) + v^3 (t_1 t_2 t_3) \end{aligned} \quad (2.6)$$

where s_i or s_j is $+1$ or -1 ; $t_1 = s_1 s_2$, $t_2 = s_2 s_3$, and $t_3 = s_3 s_4$. We have the following final expression for the partition function of graph I:

$$Z(I, N=4) = \cosh J \times \cosh J \times \cosh J \times 2 \times 2 \times 2 \times 2 \quad (2.7)$$

The above Eq. (2.6) is graphically shown in Figure 2:

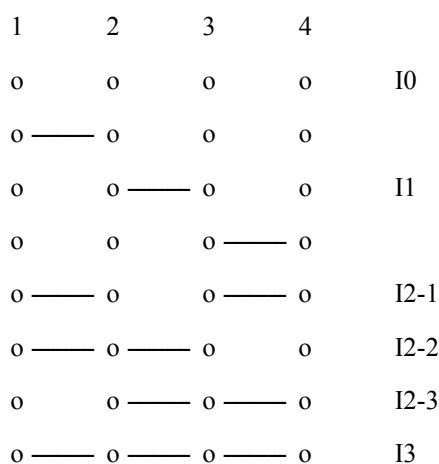


Figure 2. Graphical Explanation of Eq. (2.6).

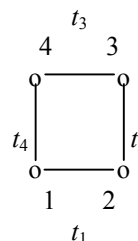


Figure 3. Graph II.

As shown in section 3, graphs I0, I1, and I2–1 are taken into consideration in the Hosoya index H , while graphs I2–2, I2–3, and I3 in the connective index C . In the case of graph II (π -electron system of cyclobutadiene, see Figure 3.) the partition function is:

$$Z(N=4) / (\cosh J)^4 = \sum_{s_1=-1}^{s_1=+1} \sum_{s_2=-1}^{s_2=+1} \sum_{s_3=-1}^{s_3=+1} \sum_{s_4=-1}^{s_4=+1} V(s), \quad (2.8)$$

where

$$V(s) = (1 + vs_1s_2)(1 + vs_2s_3)(1 + vs_3s_4)(1 + vs_4s_1) = 1 + v(t_1 + t_2 + t_3 + t_4) + v^2(t_1t_2 + t_1t_3 + t_1t_4 + t_2t_3 + t_2t_4 + t_3t_4) + v^3(t_1t_2t_3 + t_1t_2t_4 + t_1t_3t_4 + t_2t_3t_4) + v^4 t_1t_2t_3t_4, \quad (2.9)$$

where $t_4 = s_4s_1$. Finally we get the following expression for graph II, where s_i or s_j is +1 or –1 [17]:

$$Z(\text{II}, N=4) = (\cosh^4 J) \cdot 2^4 (1 + v^4) \quad (2.10)$$

A partition function itself such as Eq. (2.10) may be used as a topological index by giving values to J and v . The above equation is not discussed in the present note beyond this because we do not assume s_i or $s_j = -1$ or $+1$ but only assume s_i or $s_j = 1$ for the definitions of H and C . We define here $n(G,k)$ as the number of ways in which k bonds are chosen from graph G . The B -count polynomial $S(G,v)$ is defined as:

$$S(G, v) = \sum_{k=0}^m n(G, k) v^k \quad (2.11)$$

The bond index B is then defined:

$$B(G) = \sum_{k=0}^m n(G, k) = S(G, 1) \quad (2.12)$$

For graph G the value B is given as:

$$B = \binom{N-1}{0} + \binom{N-1}{1} + \binom{N-1}{2} + \dots + \binom{N-1}{N-1} + \binom{N-1}{N} = 2^{N-1} \quad (2.13)$$

for a tree graph, and:

$$B = 2^N \quad (2.14)$$

for a monocyclic graph. For examples in the cases of graphs I and II, $B(\text{I}) = 2^3 = 8$ and $B(\text{II}) = 2^4 = 16$. Of course the value B cannot distinguish between graphs with the same number N of vertices, *i.e.*, B gives the same value when N is fixed. Both the indices H and C can distinguish between graphs with the same number N of vertices but with different branchings and closures. This is shown in the next section.

3 HOSOYA INDEX AND CONNECTIVE INDEX

The Hosoya index was defined as follows [1]. A non-adjacent number $p(G,k)$ is the number of ways in which k bonds are so chosen from G that no two of them are connected. $p(G,0) = 1$, $p(G,1)$ = the number of bonds. The H -counting polynomial is defined as:

$$Q(G,v) = \sum_{k=0}^m p(G,k) v^k \quad (3.1)$$

The Hosoya index $H(G)$ is defined as:

$$H(G) = \sum_{k=0}^m p(G,k) = Q(G,1) \quad (3.2)$$

where m is the maximum number of k for G . In the original paper by Hosoya [1] the notation Z is used instead of H . In the present paper a topological index C (the connective index) is proposed for a graph G . Consider graph (structure) G with N vertices (electrons). The connective index C is defined as follows. The number $q(G,k)$ is the number of ways in which k connected bonds are chosen from G . The values $q(G,0)$ and $q(G,1)$ are defined as $q(G,0) = 0$ and $q(G,1) = 0$. Here partial connections among k bonds are also allowed. For example, graphs I2-2 and I2-3 are allowed for counting $q(I2,2)$, but graph I2-1 is not allowed for counting for it. The C -counting polynomial is defined as:

$$R(G,v) = \sum_{k=0}^m q(G,k) v^k \quad (3.3)$$

The connective index is defined as:

$$C(G) = \sum_{k=0}^m q(G,k) = R(G,1) \quad (3.4)$$

where m is the maximum number of k for G . Two graphs III (tree, Figure 4) and IV (non-tree, Figure 5) are shown as examples for explanation.

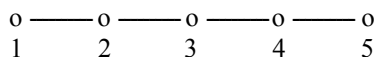


Figure 4. Graph III.

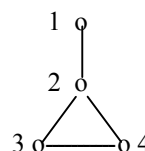


Figure 5. Graph IV.

For both graphs $q(G,0) = 0$ and $q(G,1) = 0$. The entries of $q(G,2)$ are the following pairs: graph III :1-2-3, 2-3-4, and 3-4-5; and graph IV:1-2-3, 1-2-4, 2-3-4, 2-4-3, and 3-2-4. Therefore $q(III,2) = 3$ and $q(IV,2) = 5$. There are four ways 1-2-3-4, and 2-3-4-5, 1-2. . 3-4-5, and 1-2-3. . 4-5 of choosing three bonds in which three of them are connected in the case of graph III. Then

$q(\text{III},3) = 4$. Finally we obtain:

$$R(\text{III},v) = 0 + 0v + 3v^2 + 4v^3 + v^4, \quad (3.5)$$

$$C(\text{III}) = \sum_{k=0}^{k=4} q(\text{III},k) = R(\text{III},1) = 8. \quad (3.6)$$

There are four ways, 1–2–3–4, 1–2–4–3, 2–3–4–2, and 1–2–3; 2–4, of choosing three bonds connected from graph IV. Therefore $q(\text{IV}, 3) = 4$.

$$R(\text{IV},v) = 0 + 0v + 5v^2 + 4v^3 + v^4, \quad (3.7)$$

$$C(\text{IV}) = \sum_{k=0}^{k=4} q(\text{IV},k) = R(\text{IV},1) = 10. \quad (3.8)$$

The values of the connective index are shown in Tables 1 and 2 with the values of H and B . Here the graphs represent the carbon atom skeletons of the saturated hydrocarbons given in the tables.

Table 1. $q(G, k)$ values and connective index C of tree graphs derived from saturated hydrocarbons

| N | Graph | (G) | $q(G,k)$ $k = 0, 1, 2, 3, 4, 5$ | C | H | B |
|-----|--------------------------------|---------|------------------------------------|-----|-----|-----|
| 1 | CH ₄ | (1) | 0 0 0 0 | 0 | 1 | 1 |
| 2 | C ₂ H ₆ | (2) | 0 0 0 0 | 0 | 2 | 2 |
| 3 | C ₃ H ₈ | (3) | 0 0 1 0 | 1 | 3 | 4 |
| 4 | C ₄ H ₁₀ | (4) | 0 0 3 1 | 4 | 4 | 8 |
| | C ₄ H ₁₀ | (5) | 0 0 2 1 | 3 | 5 | 8 |
| 5 | C ₅ H ₁₂ | (6) | 0 0 6 4 1 | 11 | 5 | 16 |
| | C ₅ H ₁₂ | (7) | 0 0 4 4 1 | 9 | 7 | 16 |
| | C ₅ H ₁₂ | (8) | 0 0 3 4 1 | 8 | 8 | 16 |

H and B stand for the Hosoya index and the bond index (see the text)

(1) Methane, (2) Ethane, (3) Propane, (4) 2–Methyl propane, (5) n –Butane, (6) 2, 2–di–Methyl propane, (7) 2–Methyl butane, (8) n –Pentane

Table 2. $q(G, k)$ values and connective index C of monocyclic graphs derived from saturated hydrocarbons

| N | Graph | (G) | $q(G,k)$ $k = 0, 1, 2, 3, 4, 5$ | C | H | B |
|-----|--------------------------------|---------|------------------------------------|-----|-----|-----|
| 3 | C ₃ H ₆ | (9) | 0 0 3 1 | 4 | 4 | 8 |
| 4 | C ₄ H ₈ | (10) | 0 0 5 4 1 | 10 | 6 | 16 |
| | C ₄ H ₈ | (11) | 0 0 4 4 1 | 9 | 7 | 16 |
| 5 | C ₅ H ₁₀ | (12) | 0 0 8 10 5 1 | 24 | 8 | 32 |
| | C ₅ H ₁₀ | (13) | 0 0 7 10 5 1 | 23 | 9 | 32 |
| | C ₅ H ₁₀ | (14) | 0 0 6 10 5 1 | 22 | 10 | 32 |
| | C ₅ H ₁₀ | (15) | 0 0 6 10 5 1 | 22 | 10 | 32 |
| | C ₅ H ₁₀ | (16) | 0 0 5 10 5 1 | 21 | 11 | 32 |

H and B stand for the hosoya index and the bond index, respectively

(9) Cyclopropane, (10) Methylcyclopropane, (11) Cyclobutane, (12) 1,1–di–Methylcyclopropane, (13) 1,2–di–Methylcyclopropane, (14) Ethylcyclopropane, (15) Ethylcyclobutane, (16) Cyclopentane

The number k increases when N increases in the connective index. However the number k in the Hosoya index is at most 4. This fact shows one of excellent natures, simplicity of the latter index.

The other interesting physical or mathematical characters of the Hosoya index were shown in

references [1–5,9–11].

The following equation is obtained for $n(G,k)$, $p(G,k)$, and $q(G,k)$ because of their definitions:

$$n(G,k) = p(G,k) + q(G,k) \quad (3.9)$$

Ex. $n(I,0) = 1; p(I,0) + q(I,0) = 1 + 0 = 1.$

$$n(I,1) = 3; p(I,1) + q(I,1) = 3 + 0 = 3.$$

$$n(I,2) = 3; p(I,2) + q(I,2) = 1 + 2 = 3.$$

where $n(G,k)$ is the number of ways in which k bonds are chosen from graph G .

When r is the number of bonds of a graph we have $r = N-1$ in a tree graph and $r = N$ in a monocyclic graph. The number $n(G,k)$ is expressed easily as

$$n(G,k) = \binom{r}{k} \quad (3.10)$$

Ex., $n(I,2) = \binom{3}{2} = 3!/2!1! = 3$

Therefore $q(G,k)$ can be calculated by using Eq. (3.9) and by consulting the tables of $p(G,k)$ if $n(G,k)$ is given. There is a mathematical relation among the three indices, H , C , and B because of their definitions:

$$B(G) = C(G) + H(G) \quad (3.11)$$

where $B(G) = 2^{N-1}$ in the case of tree graphs and $B(G) = 2^N$ in the case of monocyclic graphs, see Eqs. (2.13) and (2.14).

Ex. in the case of graph III $B(\text{III}) = 16; C(\text{III}) + H(\text{III}) = 8 + 8 = 16.$

Ex., in the case of graph IV $B(\text{IV}) = 16; C(\text{IV}) + H(\text{IV}) = 10 + 6 = 16.$

Then the index C can be calculated by knowing the Hosoya index H . After all the mathematical meanings and physical properties of the index C are decided by those of the Hosoya index H which has been widely investigated [1–5,9–11].

4 CONCLUSIONS

The Hosoya index and the connective index are parts of the expression for the partition function of a graph on the viewpoint of the Ising model, where the graph expresses the carbon atom skeleton of a hydrocarbon molecule. The Hosoya index H is more useful in quantitative structure–property relationships than the connective index C but the physical meaning of C was elucidated more clearly than the physical meaning of H .

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5 REFERENCES

- [1] H. Hosoya, Topological Index. A Newly Proposed Quantity Characterizing the Topological Nature of Structural Isomers of Saturated Hydrocarbons, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332–2339.
- [2] H. Hosoya, K. Kawasaki, and K. Mizutani, Topological Index and Thermodynamic Properties, I. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3415–3421.
- [3] H. Narumi and H. Hosoya, Topological Index and Thermodynamic Properties. II. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1228–1237.
- [4] H. Narumi and H. Hosoya, Topological Index and Thermodynamic Properties III, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1778–1786.
- [5] H. Narumi, H. Hosoya, and M. Katayama, Heat of Formation of Saturated Hydrocarbons and Topological Index, *Bull. Fac. Eng. Hokkaido Univ.* **1981**, *103*, 19–25.
- [6] H. Narumi, New Topological Indices for Finite and Infinite Systems, *Match* **1987**, *22*, 195–207.
- [7] I. Gutman and H. Narumi, An Inequality for the Simple Topological Index, *Coll. Sci. Papers Faculty Science Kragujevac*, **1990**, *11*, 19–22.
- [8] H. Narumi and H. Kita, Equivalent Bond Index, *Match* **1994**, *30*, 225–242.
- [9] H. Hosoya, K. Hosoi, and I. Gutman, A Topological Index for the Total π –Electron Energy, *Theoret. Chim. Acta (Berl.)* **1975**, *38*, 37–47.
- [10] H. Hosoya and M. Murakami, Topological Index as Applied to π –Electronic Systems. II. Topological Bond Order, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3512–3517.
- [11] H. Hosoya and K. Hosoi, Topological Index as Applied to π –Electronic Systems. III. Mathematical Relation among Various Bond Orders, *J. Chem. Phys.* **1976**, *64*, 1065–1073.
- [12] H. Narumi and H. Hosoya, Proof of the Generalized Expressions of the Number of Perfect Matchings of Polycube Graphs, *J. Math. Chem.* **1989**, *3*, 383–391.
- [13] H. Narumi, H. Hosoya, and H. Murakami, Generalized Expression for the Numbers of Perfect Matching of Cylindrical $m \times n$ Graphs. *J. Math. Phys.* **1991**, *32*, 1885–1889.
- [14] H. Narumi and H. Hosoya, Generalized Expression of the Perfect Matching Number of $2 \times 3 \times n$ Lattices, *J. Math. Phys.* **1993**, *34*, 1043–1051.
- [15] H. Narumi, H. Kita, and H. Hosoya, An Expression for the Perfect Matching Number of Cubic $2 \times m \times n$ Lattices and their Asymptotic Values, *J. Math. Chem.* **1994**, *16*, 221–228.
- [16] H. Narumi, H. Kita, and H. Hosoya, Expressions for the Perfect Matching Numbers of Cubic $l \times m \times n$ Lattices and their Asymptotic Values, *J. Math. Chem.* **1996**, *20*, 67–77.
- [17] For example, H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford, 1971, pp. 118–123 (Section 9. 3).

Biography

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