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Note

NOTE

Note on the Hyper-Wiener Index

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Abstract: The hyper-Wiener index *WW* of a chemical tree *T* is defined as the sum of the products $n_1 n_2$, over all pairs u, v of vertices of *T*, where n_1 and n_2 are the number of vertices of *T*, lying on the two sides of the path which connects u and v. We examine a slight modification *WWW* of the hyper-Wiener index, defined as the sum of the products $n_1 n_2 n_3$, over all pairs u, v of vertices of *T*, where n_3 is the number of vertices of *T*, lying between u and v. It is found that *WWW* correlates significantly better with various physico-chemical properties of alkanes than *WW*. Lower and upper bounds for *WWW*, and an approximate relation between *WWW* and *WW* are obtained.

Keywords: hyper-Wiener index, Wiener index, chemical trees, alkanes.

INTRODUCTION

The hyper-Wiener index is one of the recently introduced distance-based molecular structure–descriptors.[1] It was put forward[2] in 1993 and since then it has attracted much attention of theoretical chemists.[3–20] In parallel with the symbol *W* for the Wiener index,[21,22] the hyper-Wiener index is traditionally denoted by *WW*.

Let u and v be two vertices of a (chemical) tree *T* and let π_{uv} be the unique path connecting u and v. Let n_1 and n_2 be the counts of vertices lying on the two sides of π_{uv}. The vertices u and v are included in these counts, and therefore n_1 and n_2 are always greater than or equal to unity.

The hyper-Wiener index of a tree *T* is defined as

$$WW = \sum_{u,v} n_1 n_2 \qquad (1)$$

with the summation going over all pairs of vertices of *T*.

By slightly changing the right-band side of Eq. (1), one arrives at a modified version of the hyper-Wiener index, which is denoted by *WWW*:

$$WWW = \sum_{u,v} n_1 n_2 n_3 . \qquad (2)$$

Here n_3 is the number of vertices of T, lying between the endpoints of the path π_{uv}. Note that if the tree T has n vertices, then for all pairs of its vertices, $n_1 + n_2 + n_3 = n$. Further, if u and v are adjacent, then $n_3 = 0$. A mathematical reason for defining the hyper-Wiener index *via* Eq. (2) is outlined elsewhere.[23]

COMPARING THE PHYSICO-CHEMICAL APPLICABILITY OF THE OLD AND NEW HYPER-WIENER INDICES

The first question that should be asked when *WW* is modified into *WWW* is whether the new variant has a better correlating ability, as far as the physico-chemical properties of alkanes are concerned. In order to obtain comparative results on *WW* and *WWW*, the standard data base of Needham, Wei, and Seybold,[24] in which experimental values for boiling point (*BP*), molar volume (*MV*), molar refraction (*MR*), heat of evaporation (*HE*), critical temperature (*CT*), critical pressure (*CP*), surface tension (*ST*) and melting point (*MP*) of alkanes with up to 10 carbon atoms have been collected, was employed.

For *MR* and *MP* no correlation between either *WW* or *WWW* could be established, and therefore these two physico-chemical properties have not been considered any further. The remaining six sets of experimental data were correlated with polynomials of various degrees of either *WW* or *WWW*. Eventually, the optimal value p for the degree of these polynomials was established. The correlation coefficients thus obtained are given in Table I.

TABLE I. Correlation coefficients, *R(WW)* and *R(WWW)*, for the correlation between various physico-chemical properties of alkanes[24] and a p-th degree polynomial in the parameters *WW* and *WWW*, respectively. The value of p was chosen so as to be optimal from the point of view of the *F*-test, at 95 % confidence level

Property	p	*R(WW)*	*R(WWW)*
BP	5	0.9809	0.9816
MV	2	0.9687	0.9862
HE	3	0.9722	0.9804
CT	3	0.9560	0.9444
CP	5	0.9657	0.9296
ST	2	0.8310	0.8762

As can be seen from Table I, the new hyper-Wiener index *WWW* is significantly better correlated with the boiling point, molar volume, heat of evaporation, and surface tension than the older version *WW*. The new hyper-Wiener index is found to be (slightly) inferior to *WW* only in the case of the critical temperature and critical pressure.

The polynomial approximation for the boiling point could be much improved by means of the expressions:

$$\ln BP \approx A_1 \ln WW + B_1$$
$$\ln BP \approx A_2 \ln WWW + B_2$$

resulting in $R = 0.9867$ (for *WW*) and $R = 0.9911$ (for *WWW*). In these formulas *BP* is expressed in Kelvin units; by least squares fitting one obtaines $A_1 = 0.154 \pm 0.004$, $B_1 = 0.52 \pm 0.02$ and $A_2 = 0.103 \pm 0.002$, $B_1 = 5.41 \pm 0.01$.

In summary: The new hyper-Wiener index *WWW*, Eq. (2), outperforms the prevous version *WW*, Eq. (1), in correlations with almost all physico-chemical properties of alkanes. Therefore, when applying the hyper-Wiener index in QSPR and QSAR studies,[25] preference should be given to *WWW*.

ESTIMATING THE NEW HYPER-WIENER INDEX

It is first shown that the new hyper-Wiener index is bounded from both below and above by simple functions of the old hyper-Wiener index and the ordinary Wiener index:

$$WW - W \le WWW \le (n-2)(WW - W). \tag{3}$$

The summations in (1) and (2) go over all pairs of vertices. They can be divided into two parts as:

$$\sum_{u,v} = \sum_{adj} + \sum_{n,adj}$$

where $\sum_{adj}$ and $\sum_{n,adj}$ indicate summation over adjacent and non-adjacent vertex pairs.

As $n_3 = 0$ whenever the vertices u and v are adjacent, formula (2) reduces to

$$WWW = \sum_{n,adj} n_1 n_2 n_3 \tag{4}$$

If u and υ are not adjacent, then n_3 is at least 1 and at most $n - 2$. Replacing n_3 in (4) by its minimal possible value, one obtains a lower bound for *WWW*:

$$WWW \ge \sum_{n,adj} n_1 n_2 = \sum_{u,v} n_1 n_2 - \sum_{n,adj} n_1 n_2 \tag{5}$$

From Eq. (1), the first summation on the right-hand side of (5) is just *WW*. According to a well known result of Wiener,[22,26,27] the second summation on the right-hand side of (5) is equal to the Wiener index *W*. Thus one arrives at the lower bound in (3).

Replacing n_3 in (4) by its maximal possible value (= $n - 2$), one obtains

$$WWW \le (n-2) \sum_{n,adj} n_1 n_2$$

which, using the same arguments as above, leads to the upper bound in (3).

By means of an analogous, yet somewhat more complicated, reasoning, one can also deduce the following estimates:

$$\nu(\nu-1)/2 + (WW - W) \le WWW \le \nu(\nu-1)/2 + (n-3)(WW - W)$$

where ν is the number of vertices of degree one in the chemical tree T, *i.e.*, the number of methyl groups in the underlying molecule.

APPROXIMATING THE NEW HYPER-WIENER INDEX

In order ot deduce an approximate expression for the new hyper-Wiener index WWW, Eq. (2) is rewritten as:

$$WWW \approx \sum_{u,\upsilon} n_1 n_2 \langle n_3 \rangle$$

where $\langle n_3 \rangle$ is the arithmethic mean of n_3. Then,

$$WWW \approx \langle n_3 \rangle \sum_{u,v} n_1 n_2 = \langle n_3 \rangle \, WW. \tag{6}$$

In order to apply (6), the value of $\langle n_3 \rangle$ must be known (at least approximately). In order to achieve this goal, one starts with:

$$\langle n_3 \rangle = \langle n - n_1 - n_2 \rangle = n - \langle n_2 + n_3 \rangle$$

$$= n - 2 \, \langle (n_1 + n_2)/2 \rangle \approx n - 2 \, \langle \sqrt{n_1 n_2} \, \rangle$$

where the arithmetic mean of n_1 and n_2 has been replaced by their geometric mean. Using another plausible approximation, one obtains:

$$\langle \mathrm{n}_3 \rangle \approx n - 2 \sqrt{\langle n_1 n_2 \rangle} \tag{7}$$

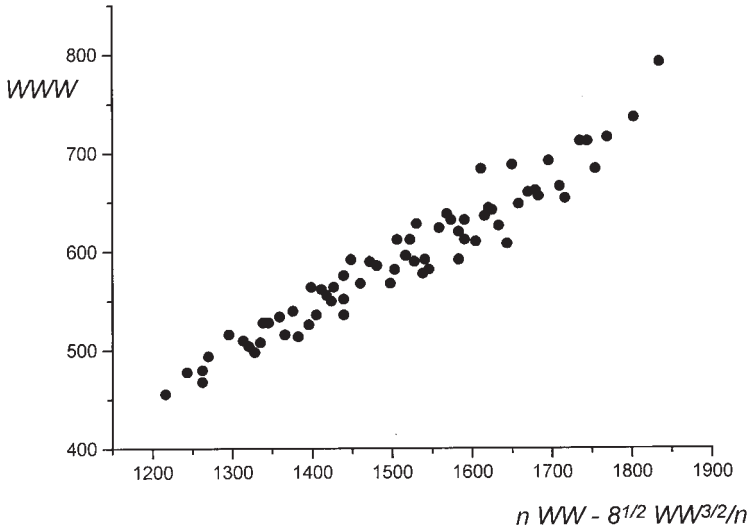

Fig. 1. The new hyper-Wiener index (WWW, Eq. (2)) *vs.* the right-hand side of Eq. (9), which is a function of the old hyper-Wiener index (WW, Eq. (1)). The data points pertain to isomeric decanes, $C_{10}H_{22}$, *i.e.*, n = 10. The correlation coefficient is 0.966.

In view of Eq. (1), the mean value of the product $n_1\ n_2$ is directly related to the hyper-Wiener index WW:

$$WW = \frac{n(n-1)}{2}\langle n_1 n_2 \rangle \tag{8}$$

where the fact that in an n-vertex graph there are $n(n-1)/2$ vertex pairs has been taken into account.

By combining the relations (6)–(8), one finally obtains the expression:

$$WWW \approx n\ WW - \frac{2\sqrt{2}}{n}\ WW^{3/2} \tag{9}$$

which relates the old and the new hyper-Wiener index.

The quality of the approximate formula (9) is seen from Fig. 1.

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ИЗВОД

БЕЛЕШКА О ХИПЕР-ВИНЕРОВОМ ИНДЕКСУ

ИВАН ГУТМАН, БОРИС ФУРТУЛА и ЈАСМИНА БЕЛИЋ

Природно-математички факултет у Крагујевцу

Хипер-Винеров индекс WW хемијског стабла T дефинисан је као сума производа $n_1\ n_2$, преко свих парова u, v чворова стабла T, где n_1 и n_2 означавају број чворова који леже са две стране пута који повезује u и v. У раду испитујемо једну модификацију WWW хипер-Винеровог индекса, дефинисану као сума производа $n_1\ n_2\ n_3$, преко свих парова u, v чворова стабла T, где n_3 означава број чворова који леже између u и v. Нађено је да је WWW значајно боље корелиран са разним физичко-хемијским особинама алкана него WW. Добивене су доње и горње границе за WWW као и једна апроксимативна релација између WWW и WW.

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