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ON TOPOLOGICAL CHARGE INDICES OF GRAPHS

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Abstract. We introduce a fast method of computing the topological charge indices of simple graphs (molecules) which does not require matrices of large sizes. For the case of trees, we give a compact formula and in the general case we obtain upper and lower bounds for the charge indices. We give concrete examples of trees and molecules with their charge indices computed using our method.

1. Introduction

Charge indices are presented for the first time by J. Galvez et al at [3] to describe the molecular charge distribution. They studied the correlation of these invariants with the dipole moment of a heterogeneous set of hydrocarbons and also the boiling temperature of alkanes and alcohols. They showed that these new charge indices are more powerful than the χ-connectivity and Wiener indices.

Quantitative structure property relationship (QSPR) is an important and applied topic in many fields of chemical science and engineering, through which various physiochemical and thermos-physical properties can be obtained based on the structure of a chemical compound [9]. The relationship between a physical property of a compound and its structure is mainly done by using topological index, which is defined by chemical graph theory. One of the first attempts in this field was the seminal work of Wiener who proposed an index in 1947 based on which boiling points of normal alkanes were correlated with a good accuracy [13]. Critical properties of normal alkanes including critical

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temperature, critical pressure, and critical volume have been successfully correlated with Padmakar-Ivan (PI) topological index [11], although its main application was found in biochemistry [6]. Concerning carbon nanostructures, these topological indices have shown their ability to predict the properties of such nano-structures. For such applications PI and Szeged indices have been obtained for some carbon nanostructures [1], [5]. Topological charge indices (TCI) have also found their applications in chemical science [10]. These indices have been proposed to evaluate the charge transfer between a pair of atoms with different electronegativity. Dipole moment of polar molecules can be evaluated using topological charge indices and compared with the experimental values. Another application of TCIs was found in perception of duplicated chemical structures in large databases [7].

There have been several graph-theoretical invariants (mostly called "topological indices" by chemists) describing various physical features of molecules, majority of them are defined based on the concept of distance. Some of the most well-known examples of such invariants are the indices introduced by Wiener, Zagreb, Balaban, Schultz, Randic and many others. These numerical invariants are studied extensively by many people and the reader can find a survey in [12].

The graph invariants (topological charge indices) G_k and J_k are describing the distribution of the electrical charge in a molecule and the most simple case for the study of these numbers is the case of hydrocarbons, where we don't need to consider weighted vertices in our graphs (not necessary to consider the electronegativity of atoms). It is also possible to consider the valence charge indices G_k^V and J_k^V for the case of heteroatoms. All these quantities are defined by employing the adjacency and distance matrices in simple connected graphs. Consequently, computing these invariants using big matrices will be hard. In this article, we introduce compact easy formulas for computing charge indices which are more practical, especially when the graph is a tree (the corresponding molecule does not contain any cycle). We apply our method to compute the charge indices of some known graphs and then some concrete molecules.

Dedication. We dedicate this work to the memory of our friend Prof. Alireza Ashrafi (vice president of the International Academy of Mathematical Chemistry) who sadly passed away on January 2023.

2. Charge indices

All graphs in this article are finite, simple, connected and they don't contain any loop. Suppose $\Gamma = (V, E)$ is a graph where

$$V = \{v_1, v_2, \ldots, v_n\}$$

is the set of vertices and E is the set of edges. We denote the degree of the vertex v_i by d_i and we assume that

$$d_1 \geq d_2 \geq \cdots \geq d_n.$$

The distance between the vertices v_i and v_j will be denoted by d_{ij} which is the length of the shortest path connecting v_i to v_j. The adjacency matrix A is an $n \times n$ matrix with $a_{ij} = 1$ if there is an edge between v_i and v_j and $a_{ij} = 0$, otherwise. We also consider the distance matrix D which is also $n \times n$

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and its (i,j)-entry is d_{ij} (we let $d_{ii}=0$ for every i). Because the electric force reduces with the inverse of the square distance, we define another matrix D^* with off-diagonal entries d_{ij}^{-2} and the diagonal entries 0. Of course all of these matrices are symmetric. Now define $M=AD^*$ and let

$$C=(M-M^T)+\Delta$$

where M^T denotes the transpose of M and Δ is the diagonal matrix with diagonal entries $d_1,d_2,\ldots,d_n$. In a molecular graph, the number c_{ij} represents electrical charge transfer from the vertex v_j to the vertex v_i. The charge index G_k is defined as

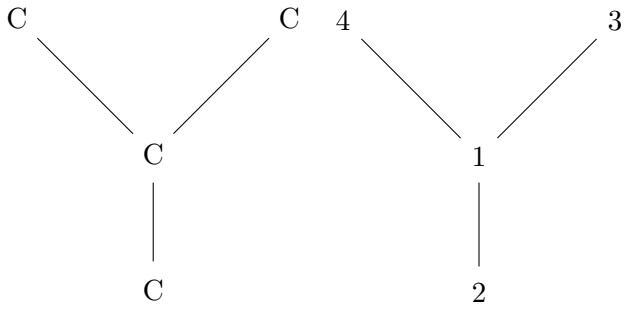
$$G_k=\sum_{i<j,d_{ij}=k}|c_{ij}|,$$

the total charge transferred among the atoms in distance k. Beside this, we define the normalized charge indices $J_k=G_k/(n-1)$. Finally, we define the algebraic charge-transfer index

$$\mu=\frac{1}{2}\sum_{i<j}c_{ij}$$

which has close connection with dipole moment of the corresponding molecule.

Example 2.1. To illustrate the above quantities, let's consider the simple molecule and its corresponding graph:



The corresponding matrices are then

$$A=\begin{bmatrix}0&1&1&1\\1&0&0&0\\1&0&0&0\\1&0&0&0\end{bmatrix},D=\begin{bmatrix}0&1&1&1\\1&0&2&2\\1&2&0&2\\1&2&2&0\end{bmatrix},D^*=\begin{bmatrix}0&1&1&1\\1&0&1/4&1/4\\1&1/4&0&1/4\\1&1/4&1/4&0\end{bmatrix}$$

and so, we have

$$M=AD^*=\begin{bmatrix}3&1/2&1/2&1/2\\0&1&1&1\\0&1&1&1\\0&1&1&1\end{bmatrix},C=\begin{bmatrix}3&1/2&1/2&/2\\-1/2&1&0&0\\-1/2&0&1&0\\-1/2&0&0&1\end{bmatrix}.$$

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As a result, we have

$$G_1 = |c_{1,2}| + |c_{1,3}| + |c_{1,4}| = 1/2 + 1/2 + 1/2 = 3/2,\ G_2 = |c_{2,3}| + |c_{2,4}| + |c_{3,4}| = 0,$$

and hence $J_1 = 1/2$ and $J_2 = 0$. Also, $\mu = 3/4$.

For $k > 1$, it is not difficult to find upper and lower bounds for G_k in terms of the vertex degrees of the graph Γ. Suppose $i < j$ and $d_{ij} = k$. We have

$$M_{ij} = (AD^*)_{ij} = \sum_{r=1}^{n} A_{ir} D^*_{rj} = \sum_{r \neq j} \frac{A_{ir}}{d^2_{rj}}. \tag{2.1}$$

If $A_{ir} = 1$ then we have $k \leq 1 + d_{rj}$ and $d_{rj} \leq k + 1$. This means that

$$\frac{d_i}{(k+1)^2} \leq M_{ij} \leq \frac{d_i}{(k-1)^2}$$

and by a similar argument

$$\frac{d_j}{(k+1)^2} \leq M_{ji} \leq \frac{d_j}{(k-1)^2}.$$

As we supposed $d_i \geq d_j$, we get

$$\frac{d_j}{(k+1)^2} \leq M_{ij}, M_{ji} \leq \frac{d_i}{(k-1)^2}$$

and hence

$$\frac{d_j}{(k+1)^2} \leq |c_{ij}| \leq \frac{d_i}{(k-1)^2}.$$

Let the set T_k be defined as

$$T_k = \{(i,j) : 1 \leq i < j \leq n, d_{ij} = k\}.$$

Then we have

$$\frac{1}{(k+1)^2} \sum_{(i,j) \in T_k} d_j \leq G_k \leq \frac{1}{(k-1)^2} \sum_{(i,j) \in T_k} d_i. \tag{2.2}$$

In the case when Γ is a tree, we can evaluate 2.1 by a simple argument. As there is a unique path between any pair of vertices, $A_{ir} = 1$ implies that $d_{rj} = k+1$ except in only one case where $d_{rj} = k-1$. So, we have

$$M_{ij} = \frac{1}{(k-1)^2} + \frac{d_i - 1}{(k+1)^2}$$

and similarly

$$M_{ji} = \frac{1}{(k-1)^2} + \frac{d_j - 1}{(k+1)^2}.$$

This shows that

$$G_k = \frac{1}{(k+1)^2} \sum_{(i,j) \in T_k} (d_i - d_j). \tag{2.3}$$

Now, we proved the following theorem, even for the case $k = 1$.

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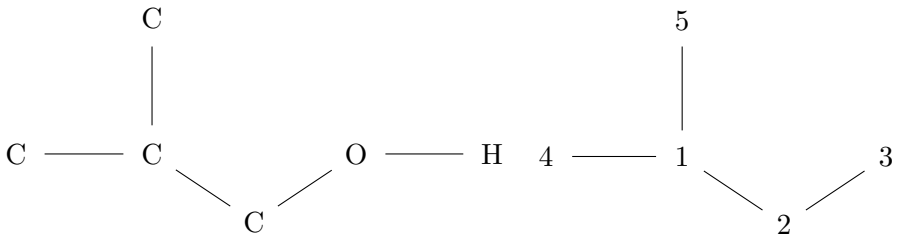
Theorem 2.2. *For any tree Γ the topological charge indices can be computed using*

$$G_k = \frac{1}{(k+1)^2} \sum_{(i,j)\in T_k} (d_i - d_j),$$

and consequently the algebraic charge transfer index is given by

$$\mu = \frac{1}{2} \sum_{k\geq 1} G_k.$$

Example 2.3. We consider isobutanol C_4OH and its corresponding graph (after removing the hydrogen atom):



Using 2.3, we see that

$$G_1 = \frac{1}{4}((3-1)+(3-1)+(3-2)+(2-1)) = 3/2,$$

$$G_2 = \frac{1}{9}((2-1)+(2-1)+(3-1)) = 4/9,$$

$$G_3 = \frac{1}{16}((1-1)+(1-1)) = 0.$$

Also we have $\mu = 35/36$.

Example 2.4. For the linear tree L_n, we have

$$G_k = \frac{2}{(k+1)^2}.$$

Note that for big enough n, we have

$$\mu \approx \frac{1}{4} + \frac{1}{9} + \frac{1}{16} + \cdots$$

which is the value of the Riemann's zeta function at 2 minus one! So we have

$$\mu = \frac{\pi^2}{6} - 1.$$

For star S_n (the tree with order $n+1$ and degree sequence $[n, 1, 1, \ldots, 1]$) we have

$$G_1 = \frac{1}{4}((n-1)(n-2))$$

and $G_k = 0$ for $k \geq 2$.

Example 2.5. We compute the charge indices of the different isomers of C_6H_{14} and as a result we have:

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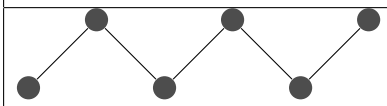
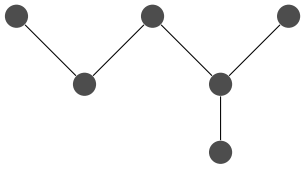
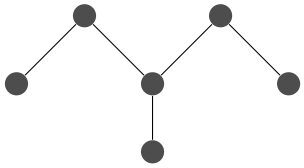
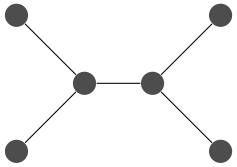
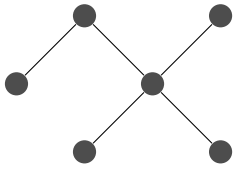
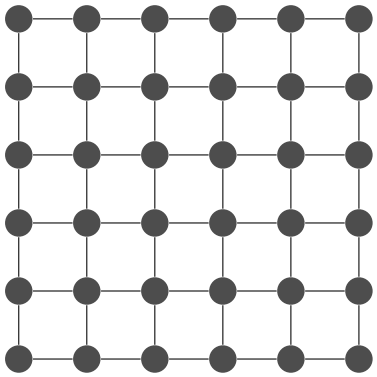
Charge indices of isomers of C_6H_{14}				
The graph	G_1	G_2	G_3	G_4
	1/2	2/9	1/8	2/25
	3/2	4/9	1/4	0
	3/2	4/9	1/8	0
	2	8/9	0	0
	3	2/3	0	0

Example 2.6. One can compute the charge indices of graphs with cycles using 2.1 as well. We consider the 2-dimensional grid Q_n as follows:



We compute the values of c_{ij} in three different cases. The reader can check the details and generalize it to any 3-dimensional grid.

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1. Let both vertices be inside the grid. In this case we have $c_{ij} = 0$.
2. Let the vertex i be in the boundary and j be inside. Then

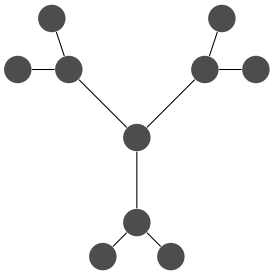
$$c_{ij} = \frac{-2}{(k+1)^2}.$$

3. Let both vertices be on the boundary. Then $c_{ij} = 0$.

As a result, we have

$$G_k = \frac{4n(n-1)^2}{(k+1)^2}.$$

Example 2.7. We consider a rooted tree T_n with diameter $2n$ such that the degree of each inner vertex is 3.



Note that

$$|T_n| = 1 + 3 \times 2^0 + 3 \times 2^1 + \cdots + 3 \times 2^{n-1} = 1 + 3(2^n - 1).$$

The number of leaves (vertices of degree one) is equal to $l_n = 3 \times 2^{n-1}$. In order to compute G_k we need to consider all paths of length k. For any two inner vertices i and j we have $d_i - d_j = 3 - 3 = 0$ and for any two leaves $d_i - d_j = 1 - 1 = 0$. Hence, we have to consider only the case when the vertex indexed by i is a leaf and the vertex j is inner. In this case we have

$$G_k = \frac{1}{(k+1)^2} \times \frac{1}{2} N_k \times (3-1) = \frac{1}{(k+1)^2} N_k$$

where N_k is the number of all paths of length k connecting a leaf to an inner vertex. It is easy to see that

$$N_1 = N_2 = l_n, N_3 = N_4 = 2l_n, N_5 = N_6 = 2^2 l_n, \ldots$$

and so, in general $N_{2r-1} = N_{2r} = 2^{r-1} l_n = 3 \times 2^{n+r-2}$. Therefore, for any r

$$G_{2r-1} = \frac{3 \times 2^{n+r-2}}{(2r)^2}, \; G_{2r} = \frac{3 \times 2^{n+r-2}}{(2r+1)^2}.$$

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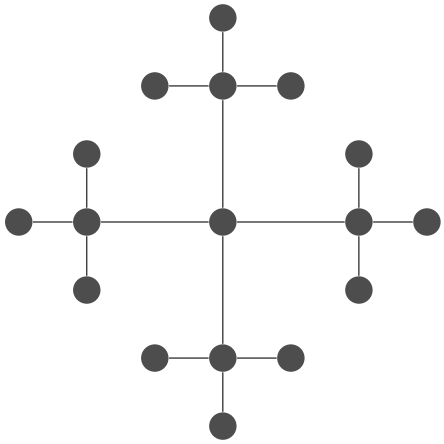
Hence, we have

$$\begin{aligned}\mu &= \frac{1}{2}(G_1 + G_2 + \cdots + G_{2n-1}) \\ &= \frac{1}{2}(\frac{3\times 2^{n-1}}{2^2} + \frac{3\times 2^{n-1}}{3^2} + \frac{3\times 2^n}{4^2} + \frac{3\times 2^n}{5^2} + \cdots \\ &\quad + \frac{3\times 2^{2n-3}}{(2(n-1))^2} + \frac{3\times 2^{2n-3}}{(2(n-1)+1)^2} + \frac{3\times 2^{2n-2}}{(2n)^2}) \\ &= 3\times 2^{n-2}\sum_{r=2}^{2n}\frac{2^{[r/2]-1}}{r^2}.\end{aligned}$$

Note that, here $[r/2]$ means the integral part of $r/2$.

Example 2.8. We compute the charge indices corresponding to any rooted tree with inner degrees equal to a constant a and the diameter $2n$. For example, the following rooted tree $F_2(n)$ is the ball of radius n in the Cayley graph of the free group of rank 2. In other words, $F_2(n)$ is a rooted tree such that the degree of any inner vertex is 4.



We denote by $R_a(n)$ a rooted tree of diameter $2n$ and inner degrees a. Let l_n denote the number of leaves in this tree. Obviously, we have $l_n = (a-1)l_{n-1}$ and $l_1 = a$, hence $l_n = a(a-1)^{n-1}$. Consequently

$$\begin{aligned}|R_a(n)| &= 1 + l_1 + l_2 + l_3 + \cdots + l_n \\ &= 1 + a + a(a-1) + a(a-1)^2 + \cdots + a(a-1)^{n-1} \\ &= 1 + a\frac{(a-1)^n - 1}{a-2}.\end{aligned}$$

In order to compute the charge indices G_k, we have to consider all paths of length k with a leaf as the initial vertex. We denote the number of all such paths by N_k. We have

$$N_{2r-1} = N_{2r} = (a-1)^{r-1}l_n = a(a-1)^{n+r-1}$$

and hence

$$G_{2r-1} = \frac{1}{2(2r)^2}a(a-1)^{n+r-2}, \quad G_{2r} = \frac{1}{2(2r+1)^2}a(a-1)^{n+r-2}.$$

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3. **Valence charge indices**

In the case when the molecule contains heteroatoms, the charge distribution can be described by the valence charge indices much better. In this case one can consider the electronegativity of atoms in the adjacency matrix A. For an atom X, the electronegativity is denoted by χ_X, so that χ_C is the electronegativity of carbon. Again, for a given molecule, we label the vertices in such a way that the degree sequence is non-increasing. In the adjacency matrix A we put $A_{ii} = \lambda_i$ which is equal to $\chi_X - \chi_C$, the difference between the electronegativity of the corresponding atom and that of carbon (as usual we remove hydrogen atoms). The matrices D, D^*, Mb and C are defined as in the previous section. So, for any i and j in the distance k, we have

$$M_{ij} = \frac{\lambda_i}{k^2} + \sum_{r\neq j, A_{ir}=1} \frac{1}{d_{rj}^2}. \tag{3.1}$$

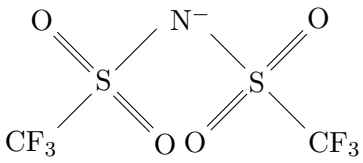
Of course, when the graph is a tree and $k > 1$, we have

$$M_{ij} = \frac{\lambda_i}{k^2} + \frac{1}{(k-1)^2} + \frac{d_i - 1}{(k+1)^2}.$$

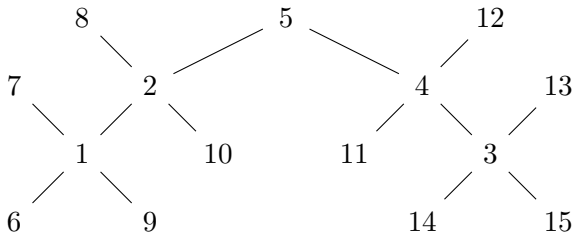
As a result, for a tree, we have

$$c_{ij} = \frac{\lambda_i - \lambda_j}{k^2} + \frac{d_i - d_j}{(k+1)^2}. \tag{3.2}$$

Example 3.1. Consider the following ionic liquid:



So, the corresponding graph is



Pauling electronegativity of the above atoms are given in the following table:

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Pauling electronegativity		
Atom	e.neg	λ
O	3.44	0.89
F	3.98	1.43
C	2.55	0
N	3.04	0.49
S	2.58	0.03

Using 3.2, we compute the absolute values of c_{ij} for $i < j$. The results are collected in the following table rounded up to 10^{-2}. Note that in the table, i is the number of row which changes between 1 and 14 and j is the number of column which changes between 2 and 15.

The values of $\lvert c_{ij}\rvert$ for $i < j$													
0.03	0.00	0.00	0.10	0.68	0.68	0.56	0.68	0.56	0.06	0.06	0.03	0.03	0.03
	0.00	0.00	0.04	0.02	0.02	0.11	0.02	0.11	0.09	0.09	0.03	0.03	0.03
		0.03	0.10	0.08	0.08	0.06	0.08	0.06	0.11	0.11	0.68	0.68	0.68
			0.04	0.03	0.03	0.09	0.03	0.09	0.11	0.11	0.02	0.02	0.02
				0.04	0.04	0.01	0.04	0.01	0.01	0.01	0.04	0.04	0.04
					0.00	0.06	0.00	0.06	0.02	0.02	0.00	0.00	0.00
						0.06	0.00	0.06	0.02	0.02	0.00	0.00	0.00
							0.06	0.00	0.00	0.12	0.02	0.02	0.02
								0.06	0.02	0.02	0.00	0.00	0.00
									0.00	0.00	0.02	0.02	0.02
										0.00	0.06	0.06	0.06
											0.06	0.06	0.06
												0.00	0.00
													0.00

Using this table, it is quite easy to compute the valence charge indices G_k^V: it is enough to apply the following algorithm:

1- Put $G_k^V = 0$ and $i = 1$.
2- Find all paths $i - - - j$ with length k and $i < j$.
3- For each such a path put $G_k^V := G_k^V + |c_{ij}|$.
4- If $i < 14$ then put $i := i + 1$ and go to 2.
5- If $i = 14$ return G_k^V.

The final result is given below:

$$G_1^V \approx 4.66,\ G_2^V \approx 1.94,\ G_3^V \approx 1.32,\ G_4^V \approx 0.42,\ G_5^V \approx 0.57,\ G_6^V \approx 0.$$

http://dx.doi.org/10.22108/toc.2023.137285.2062

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