Wiener Number as an Immanant of the Laplacian of Molecular Graphs

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In this work, we show that the Wiener number of an acyclic molecule may be expressed as a linear function of a hook immanant of the Laplacian matrix associated with the molecule. This relation leads to a new interpretation of the Wiener number as a weighted sum of matchings in the molecular graph of acyclic compounds. The connection between the Wiener number and immanants may pave the way for more use of algebraic tools in the study of the Wiener number.

1. INTRODUCTION

The Wiener number originated from the work of Wiener[1] in 1947 as a topological index to study the relation between molecular structure and physical and chemical properties of certain hydrocarbon compounds. Since then, much progress has been made in understanding the properties of the Wiener number and its applications by numerous investigators. Nice surveys of the subject may be found in the articles of Nikolić et al.[2] and Gutman et al.[3] and the many references contained in them. Connections between the Wiener number and the Laplacian and adjacency matrix of the underlying graph have been made in recent studies.[2−5] In particular, the Wiener number of an acyclic molecular graph may be expressed in terms of the Laplacian graph eigenvalues. Here we consider an algebraic function of the Laplacian matrix called an immanant that turns out to be equivalent to the Wiener number. Immanants are matrix functions that include the familiar determinant and permanent. If $A = [a_{ij}]$, then the determinant is defined by

$$\det(A) = \sum_{\sigma \in S_n} \mathrm{sgn}(\sigma) \prod_{i=1}^{n} a_{i\sigma(i)}$$

where $\mathrm{sgn}(\sigma) = 1$ or -1 corresponding to an even or odd permutation, respectively, and the permanent is defined by

$$\mathrm{per}(A) = \sum_{\sigma \in S_n} \prod_{i=1}^{n} a_{i\sigma(i)}$$

The immanant d_λ associated with the character χ_λ of the symmetric group S_n is defined as

$$d_\lambda(A) = \sum_{\sigma \in S_n} \chi_\lambda(\sigma) \prod_{i=1}^{n} a_{i\sigma(i)}$$

2. IMMANANTS OF LAPLACIAN MATRIX

Let G be a graph with n vertices and let $L(G) = [l_{ij}]$ denote its Laplacian matrix. Let χ_λ be an irreducible character of the symmetric group indexed by a partition λ of n (for review and references on characters and representation theory, see refs 6 and 7). The immanant of the Laplacian matrix is

$$d_\lambda(L(G)) = \sum_{\sigma \in S_n} \chi_\lambda(\sigma) \prod_{i=1}^{n} l_{i\sigma(i)} \qquad (1)$$

When the partition $\lambda = (1^n)$, $\chi_{(1^n)}$ is the alternating character and $d_{(1^n)}(L(G)) = \det(L(G))$ is the determinant of the matrix $L(G)$. When the partition $\lambda = (n)$, $\chi_{(n)}$ is the trivial character and $d_{(n)}(L(G)) = \mathrm{per}(L(G))$ is the permanent of the matrix $L(G)$. When the partition λ is of the form $\lambda = (k, 1^{n-k})$, we call $d_{(k,1^{n-k})}$ a hook immanant, as the Young tableau associated with the partition resembles a hook. To simplify the notation, we shall write χ_k for $\chi_{(k,1^{n-k})}$ and d_k for $d_{(k,1^{n-k})}$.

In the case where the graph G is a tree, say T, the computation in eq 1 simplifies greatly. Let T be a tree on n vertices with vertex set $V(T) = \{v_1, v_2, ..., v_n\}$ and edge set $E(T)$. The Laplacian matrix, $L(T) = [l_{ij}]$, is defined by

$$l_{ij} = \begin{cases} \deg_T(v_i) & \text{if } i = j \\ -1 & \text{if } \{v_i, v_j\} \in E(T) \\ 0 & \text{otherwise} \end{cases}$$

where $\deg_T(v)$ denotes the degree of the vertex v in T. We may drop the subscript T if it is clear from the context which tree we are referring to. Since T has no cycles, $\prod_{i=1}^{n} l_{i\sigma(i)} = 0$ if, in cycle notation, σ has a cycle of length 3 or more. For permutations σ containing cycles of length at most 2, $\prod_{i=1}^{n} l_{i\sigma(i)} = 0$ if, for some $i \neq \sigma(i)$, $\{v_i, v_{\sigma(i)}\} \notin E(T)$. This shows that, in the calculation of $d_\lambda(L(T))$, many of the terms are zero. This consideration motivates the concept of weighted j-matching number in a tree.

A j-matching $M \subseteq E(T)$ is a subset of j independent edges in T. That is, no two of these edges share a common vertex. We use the notation $v \in M$ to mean that the vertex v is incident with some edge in M, and $v \notin M$ shall mean that the vertex v is not incident to any edge in M. For $j = 0, 1, ..., \lfloor n/2 \rfloor$, the *weighted j-matching number* of T is defined to be

$$m_T(j) = \sum_{M} \prod_{v \notin M} \deg_T(v)$$

where the sum is taken over all possible j-matchings M of the tree T. If all vertices are incident to edges in M, we

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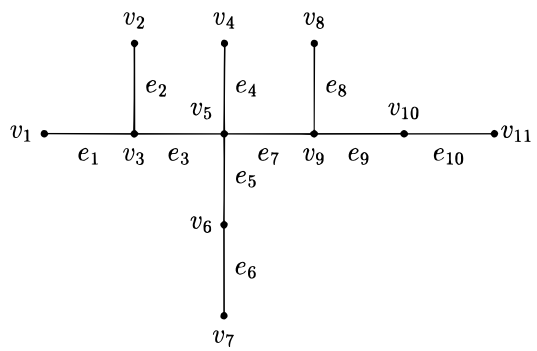
Table 1

matching	contribution to $m_T(1)$	matching	contribution to $m_T(1)$
$\{e_1\}$	48	$\{e_6\}$	72
$\{e_2\}$	48	$\{e_7\}$	12
$\{e_3\}$	12	$\{e_8\}$	48
$\{e_4\}$	36	$\{e_9\}$	24
$\{e_5\}$	18	$\{e_{10}\}$	72

treat the empty product to be 1. Note that $m_T(j) \geq 0$ and $m_T(0) = \prod \deg_T(v)$. We set $\chi_\lambda(j) = \chi_\lambda(\sigma)$, where σ is a permutation with cycle type $(2^j, 1^{n-2j})$. The preceding discussion allows us to conclude that

$$d_\lambda(L(T)) = \sum_{j=0}^{[n/2]} \chi_\lambda(j)\, m_T(j) \qquad (2)$$

We illustrate the computation of $m_T(j)$ with an example for the molecular graph T of 2,3,4-trimethyl-3-ethylhexane.



Graph T

The vertices of T are labeled $v_1, v_2, ..., v_{11}$ while the edges are labeled $e_1, e_2, ..., e_{10}$. We denote the degree of vertex v_i by $\deg(v_i)$. The term $m_T(0)$ is simply the product of the degrees of the vertices, namely

$$m_T(0) = \deg(v_1)\deg(v_2) \ldots \deg(v_{11}) = 1 \times 1 \times 3 \times 1 \times 4 \times 2 \times 1 \times 1 \times 3 \times 2 \times 1 = 144$$

For the term $m_T(1)$ we sum the contributions from all matchings of size 1. Every edge is a matching of size 1. The contribution from the matching, say $\{e_3\}$, is the product of all the degrees of vertices not incident to the edge e_3; that is

$$\deg(v_1)\deg(v_2)\deg(v_4)\deg(v_6)\deg(v_7)\deg(v_8)\deg(v_9)\deg(v_{10})\deg(v_{11}) = 12$$

Table 1 gives the contributions of each edge in T.

Summing over all the matchings of size 1 gives

$$m_T(1) = 48 + \ldots + 72 = 390$$

For $m_T(2)$, we sum all the contributions from matchings of size 2. For example, the contribution from the matching $\{e_1, e_8\}$ is the product of the degrees of the seven vertices not incident to e_1 or e_8, namely

$$\deg(v_2)\deg(v_4)\deg(v_5)\deg(v_6)\deg(v_7)\deg(v_{10})\deg(v_{11}) = 16$$

Summing over all possible matchings of size 2 gives $m_T(2) = 386$. In a similar fashion we compute $m_T(3) = 170$, $m_T(4) = 32$, and $m_T(5) = 2$.

The next result expresses a relationship between the degrees of vertices and the distances between the vertices.

Lemma 2.1. Let T be a tree with vertex set $V(T) = \{v_1, v_2, ..., v_n\}$. Fix a vertex v_i of T. Then

$$\sum_{j=1}^{n} \deg(v_j)\, d(v_i,v_j) = 2\sum_{j=1}^{n} d(v_i,v_j) - (n-1)$$

where $d(v_i,v_j)$ is the distance between v_i and v_j in the tree; that is, $d(v_i,v_j)$ is the number of edges along the unique path joining the vertices v_i and v_j.

Proof. Using a combinatorial argument, we prove the equivalent statement

$$\sum_{j=1}^{n} d(v_i,v_j) = \sum_{j=1}^{n} (\deg(v_j) - 1) d(v_i,v_j) + n - 1$$

We root T at v_i. Any vertex v_j is connected to v_i by a unique path. Let v_k be the vertex in the path closest to v_j. Then

$$d(v_i,v_j) = d(v_i,v_k) + 1$$

Call v_j a child of v_k. Denote the set of children of v_k by $C(v_k)$. Then

$$\sum_{v_j \in C(v_k)} d(v_i,v_j) = \begin{cases} (\deg(v_k) - 1)d(v_i,v_k) + \deg(v_k) - 1 & \text{if } k \neq i \\ \deg(v_i) & \text{if } k = i \end{cases}$$

Now, when we sum over all v_k, we get

$$\sum_{j=1}^{n} d(v_i,v_j) = \sum_{k=1}^{n} \sum_{v_j \in C(v_k)} d(v_i,v_j)$$

$$= \sum_{k \neq i} (\deg(v_k) - 1) d(v_i,v_k) + \sum_{k \neq i} (\deg(v_k) - 1) + \deg(v_i)$$

$$= \sum_{k=1}^{n} (\deg(v_k) - 1) d(v_i,v_k) + n - 1$$

Remarks. (1) The expression $\sum_{j=1}^{n} \deg(v_j)\, d(v_i,v_j)$ in Lemma 2.1 is related to another quantity

$$S = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} (\deg(v_i) + \deg(v_j)) d(v_i,v_j)$$

that is part of the Schultz molecular topological index.[8] The result of Lemma 2.1 and the computations in its proof may be inferred from the discussion by Gutman[9] and Klein et al.[10]

(2) A Schultz-type topological index

$$S^* = \sum_{i=1}^{n}\sum_{j=1}^{n} \deg(v_i)\deg(v_j)\, d(v_i,v_j)$$

was studied by Gutman,[8] where he obtained the formula

$$S^* = 8W - 2(2n-1)(n-1)$$

which is the main focus of the computation in eq 4 of the proof of Theorem 2.2.

We are now ready to establish a relation between the Wiener number and the third hook immanant d_3. Recall that the Wiener number is the sum of all the distances between pairs of vertices in the tree.

Theorem 2.2. Let T be a tree on n vertices. Then

$$d_3(L(T)) = 4\sum_{i=1}^{n}\sum_{j>i}(d(v_i,v_j) - 1) = 4W - 2n(n-1) \quad (3)$$

where W is the Wiener number of T.

Proof. From eq 29 in ref 11,

$$d_3(A) = \sum_{i=1}^{n}\sum_{j>i}(a_{ii}a_{jj} + a_{ij}a_{ji}) \det A(i,j) - d_2(A)$$

where $A(i,j)$ is the principal submatrix of A obtained by deleting the ith and jth rows and columns. When $A = L(T)$, it is known[12] that $d_2(L(T)) = 2(n-1)$. By the All Minors Matrix Tree Theorem,[13] $\det(L(T)(i,j))$ is the number of spanning forests rooted at v_i and v_j. In this case, this is equal to $d(v_i,v_j)$. Also when $i \neq j$

$$a_{ij}a_{ji} = \begin{cases} 1 & \text{if } \{v_i, v_j\} \in E(T) \\ 0 & \text{otherwise} \end{cases}$$

Therefore, applying Lemma 2.1 to the expression for $d_3(L(T))$ above, we have

$$d_3(L(T)) = \frac{1}{2}\sum_{i=1}^{n} \deg(v_i) \sum_{j=1}^{n} \deg(v_j)\, d(v_i,v_j) + \sum_{\{v_i,v_j\}\in E(T)} d(v_i,v_j) - 2(n-1)$$

$$= \frac{1}{2}\sum_{i=1}^{n}\deg(v_i)(2\sum_{j=1}^{n}d(v_i,v_j) - (n-1)) - (n-1)$$

$$= \sum_{j=1}^{n}\sum_{i=1}^{n}\deg(v_i)\, d(v_i,v_j) - n(n-1) \quad (4)$$

$$= \sum_{j=1}^{n}(2\sum_{i=1}^{n}d(v_i,v_j) - (n-1)) - n(n-1)$$

$$= 4\sum_{i=1}^{n}\sum_{j>1}d(v_i,v_j) - 2n(n-1)$$

$$= 4\sum_{i=1}^{n}\sum_{j>1}(d(v_i,v_j) - 1)$$

$$= 4W - 2n(n-1)$$

We see that

$$W = \frac{d_3(L(T)) + 2n(n-1)}{4}$$

3. WIENER NUMBER AS A WEIGHTED SUM OF MATCHINGS

Several methods for the computation of the Wiener number are known.[2,4,14−19] Of particular interest to chemists are those that can be carried out by hand. In this section we derive a computation based on weighted matchings in the graph. Rewriting eq 3 in Theorem 2.2 using eq 2, we have

Table 2

	0	1	2	3	4	5	6
3	1	1					
4	3	1	−1				
5	6	0	−2				
6	10	−2	−2	2			
7	15	−5	−1	3			
8	21	−9	1	3	−3		
9	28	−14	4	2	−4		
10	36	−20	8	0	−4	4	
11	45	−27	13	−3	−3	5	
12	55	−35	19	−7	−1	5	−5

$$W = \frac{1}{4}(d_3(L(T)) + 2n(n-1)) \quad (5)$$

$$= \frac{1}{4}\left(\sum_{j=0}^{[n/2]}\chi_3(j)\, m_T(j) + 2n(n-1)\right)$$

In order to use eq 5, we need to have a formula for the value of the character $\chi_3(j)$ for $j = 0, 1, ..., [n/2]$. The formula for $\chi_3(j)$ depends on n, and we shall use $\chi_3^n(j)$ to denote $\chi_3(j)$ to reflect this dependence. We recall that $\chi_1^n(j) = \chi_{(1^n)}(j) = (-1)^j$ for $0 \le j \le [n/2]$. The quantity $\chi_3^n(j)$ may be computed by a recursive formula obtained from the Murnaghan−Nakayama (M-N) Rule (see page 177 in ref 6).

$$\chi_3^n(j) = \chi_1^{n-2}(j-1) - \chi_3^{n-2}(j-1) = (-1)^{j-1} - \chi_3^{n-2}(j-1) \quad (6)$$

Using the recursive formula in eq 6 and the values of $\chi_3^n(j)$ for $n = 3$ and 4, the values for $\chi_3^n(j)$ in Table 2 are easily generated.

An exact formula for $\chi_3^n(j)$ is also known.[20] It is given by

$$\chi_3(j) = \chi_3^n(j) = (-1)^{j-1}\left(j - \binom{n-2j-1}{2}\right)$$

$$= (-1)^j\left(\frac{1}{2}(n-2j-1)(n-2j-2) - j\right) \quad (7)$$

As an example for the use of formula 5, we compute the Wiener number for the molecular graph T of 2,3,4-trimethyl-3-ethylhexane. From section 2 we have $m_T(0) = 144$, $m_T(1) = 390$, $m_T(2) = 386$, $m_T(3) = 170$, $m_T(4) = 32$, and $m_T(5) = 2$, and Table 2 gives $\chi_3^{11}(0) = 45$, $\chi_3^{11}(1) = -27$, $\chi_3^{11}(2) = 13$, $\chi_3^{11}(3) = -3$, $\chi_3^{11}(4) = -3$, and $\chi_3^{11}(5) = 5$. The Wiener number for T is

$$W = \frac{1}{4}(\sum_{j=0}^{5}\chi_3^{11}(j)\, m_T(j) + 2(11)(11-1))$$

$$= \frac{1}{4}(45(144) - 27(390) + 13(386) - 3(170) - 3(32) + 5(2) + 220)$$

$$= 148$$

which agrees with the value obtained on page 655 in ref 3.

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