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Clar Covers and Zhang-Zhang Polynomials of Zigzag and Armchair Carbon Nanotubes

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Abstract

We derive here compact formulas for the Zhang-Zhang (ZZ) polynomials of two classes of finite open-ended carbon nanotubes: zigzag nanotubes $(n, 0)$ of length d and armchair nanotubes (n, n) of length d. For zigzag nanotubes, the underlying Clar cover theory is trivial; in contrast, for armchair nanotubes, the Clar theory is complex and abundant in results. The ZZ polynomial formulas have been obtained using the interface theory of benzenoids and the transfer matrix methodology.

1 Introduction

The mathematical Clar theory of open-ended carbon nanotubes (*aka* tubulenes) received little attention in the literature [1, 25, 58, 91]. In most cases, Clar theory was used as a tool for defining small primitive unit cells used for quantum chemical modeling of metallic character and chemical reactivity of nanotubes [3–5, 52, 63–67, 74, 80, 97], the characteriza-

tion, distribution and visualization of the Kekulé and Clar regions in nanotubes [59, 62, 63], and the analysis of aromaticity patterns [55, 60, 61]. In contrast, the Clar theory of capped nanotubes (formally belonging to spherical carbon nanostructures, i.e., fullerenes) attracted more attention, focusing predominantly on the determination of the Clar number [22, 68], and on the enumeration and characterization of the nanotube caps [7, 23]. From the practical viewpoint, the most convenient way to construct and enumerate Clar covers is associated with the concept of the Zhang-Zhang (ZZ) polynomial [1, 9, 92–94], which can be useful for various chemical applications [21,28,77,90]. Note that the ZZ polynomial theory of open-ended carbon nanotubes has been never developed up-to-date.

The mathematical Kekulé theory of carbon nanotubes is well-developed for all types of carbon nanotubes: zigzag, armchair, chiral, capped, and toroidal [38, 40, 54, 56, 76, 78, 79, 82, 83]. As mentioned earlier, rather little is known about the Clar theory of nanotubes. The most effort was invested in the determination of the Clar number Cl of open-ended carbon nanotubes, i.e., the maximal number of Clar sextets [17] that can be simultaneously placed in the hexagonal network of nanotubes without violating the chemical bonding principles. The k-resonance theory of open-ended nanotubes initiated by Zhang and Wang [91] and further developed by Guo [25] demonstrated that the Clar number of zigzag nanotubes have $Cl = 0$, while for the armchair nanotubes, one has $Cl > 0$. The aromaticity of various open-ended nanotubes was studied by Lukovits and collaborators [54, 56–58].

In the current paper, we attempt to fill the gap in the literature by developing the theory of Clar covers for two classes of carbon nanotubes, zigzag nanotubes $(n, 0)_d$ and armchair nanotubes $(n, n)_d$. The Clar theory of chiral nanotubes $(n, m)_d$ with $n > m > 0$ seems to be considerably more complicated and we do not attempt to explicate it in the current study.

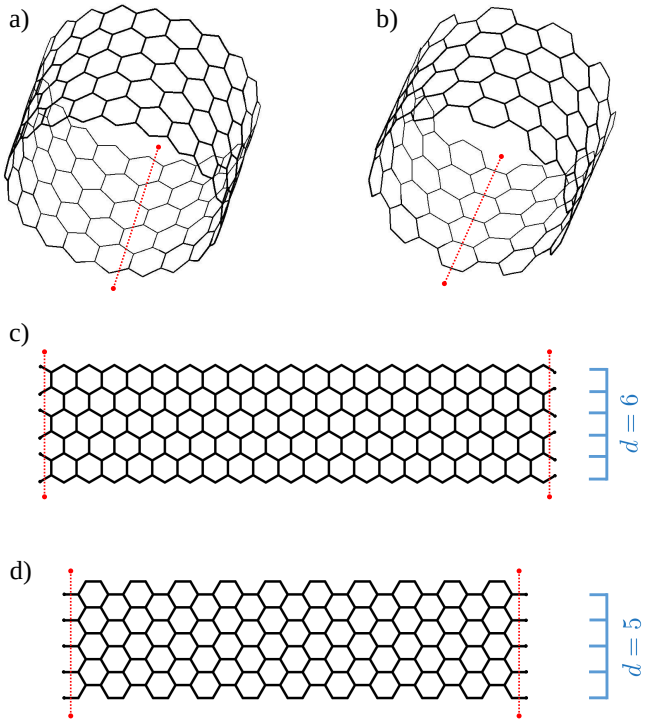


Figure 1. Examples of a) zigzag nanotube $(n, 0)_d$ (here $n = 20$ and $d = 6$) and b) armchair nanotube $(n, n)_d$ (here $n = 10$ and $d = 5$). The dotted (red) line symbolizes a scission line allowing us to represent $(n, 0)_d$ and $(n, n)_d$ as planar structures shown in c) and d), respectively. Within these flat representations, pairs of edges that the scission line intersects are considered equivalent and thus should be identified with each other.

2 Clar covers and ZZ polynomials of carbon nanotubes

Open-ended carbon nanotubes are tubular aromatic hydrocarbons consisting of fused benzene rings arranged on the surface of a cylinder. (For examples of such systems, see Figs. 1 and 3.) Each carbon atom has three carbon neighbors, except for the carbon atoms located at the ends of the nanotube; those are bonded to two other carbons and a hydrogen to satisfy the chemical bonding principles of aromatic hydrocarbons. The cor-

responding molecular graph **G**, whose vertices represent the carbon atoms and whose edges represent the carbon-carbon bonds, is part of some regular hexagonal tessellation of a cylinder. A spanning subgraph **K** of **G** is called a Kekulé structure, if every component of **K** is K_2 (a complete graph on two vertices). Similarly, a spanning subgraph **C** of **G** is called a Clar cover, if every component of **C** is K_2 or C_6 (a cycle of girth 6). The number $\mathcal{K} \equiv \mathcal{K}(\mathbf{G})$ of distinct Kekulé structures that can be constructed for **G** is called the Kekulé count; similarly, the number $\mathcal{C} \equiv \mathcal{C}(\mathbf{G})$ of distinct Clar covers that can be constructed for **G** is called the Clar count. The number of the C_6 components in **C** is called the order of **C** and is denoted as ord(**C**). Clearly, every Kekulé structure of **G** is a Clar cover of **G** of order 0. The maximal number of the C_6 components that can be simultaneously accommodated in **G** is called the Clar number of **G** and is denoted as $Cl \equiv Cl(\mathbf{G})$. The Clar covers of order Cl are referred to as the Clar structures of **G** [17].

The presented graph-theoretical terminology has lexical equivalents in the language of chemistry. This relationship is briefly explained in this paragraph. K_2 is referred to as the double bond; it is depicted as a double line segment  located over a selected molecular graph edge. C_6 is referred to as the aromatic sextet or the Clar sextet [17]; it is depicted as a circle  located in the center of a selected hexagon. Similarly, a Kekulé structure **K** is referred to as a resonance structure of **G**, and a Clar cover **C**, as a generalized resonance structure of **G**. While the content of the current work is presented predominantly in the graph-theoretical language, we find it convenient at times to resort to chemical notation, particularly in the graphical representations of Clar covers.

The problem of enumeration of Clar covers of aromatic hydrocarbons received considerable attention in the literature. Probably the most comprehensive approach to Clar theory of benzenoids was introduced almost 30 years ago by Zhang and Zhang [92–94], who defined the so-called Clar covering polynomial

$$ZZ\,(\mathbf{G}, x) \quad = \quad \sum_{\mathbf{C}} x^{\mathrm{ord}(\mathbf{C})} \tag{1}$$

where the summation runs over all conceivable Clar covers **C** of **G**. This polynomial, from the names of its inventors most often referred to in the literature as the Zhang-Zhang polynomial [1] or briefly as the ZZ polynomial [9], formally constitutes the generating function

$$ZZ\left(\mathbf{G},x\right) \quad = \quad \sum_{k=0}^{Cl} c_k x^k \tag{2}$$

for the sequence $(c_0, c_1, \ldots, c_{Cl})$, where c_k denotes the number of distinct Clar covers of order k that can be constructed for **G**. The ZZ polynomial conveniently summarizes (see Theorem 2 of [92]) the most important topological invariants of **G**

$$\mathcal{K} \quad = \quad c_0 = ZZ\left(\mathbf{G},x\right)\Big|_{x=0} \tag{3}$$

$$\mathcal{C} \quad = \quad c_0 + c_1 + \cdots + c_{Cl} = ZZ\left(\mathbf{G},x\right)\Big|_{x=1} \tag{4}$$

$$Cl \quad = \quad \text{degree}\left(ZZ\left(\mathbf{G},x\right)\right) \tag{5}$$

$$h_1 \quad = \quad c_1 = \frac{d\,ZZ\left(\mathbf{G},x\right)}{dx}\Big|_{x=0} \tag{6}$$

where h_1 is the first Herndon number of **G** [36]. The main advantage of using the ZZ polynomials lies in the underlying recurrence relations [92] allowing one for efficient computation of ZZ polynomials using partial covering decomposition algorithms [1,9,12]. Such calculations can be performed much faster than the determination of a single topological invariant. In particular, the recently reported ZZPolyCalc software [75] can be used for very robust determination of ZZ polynomials of large molecular graphs (planar, tubular, spherical, or toroidal), which may contain even thousands of vertices (atoms); the efficiency of the implementation relies on a hash-indexed library of repeated subgraph motifs occurring during the recursive decomposition. These codes has been used for tabulation of the ZZ polynomials for all the isomers of (5,6)-fullerenes containing up to 70 carbon atoms [84]. Interestingly, all these 30579 ZZ polynomials are distinct and can be readily used as a unique label for differentiating between

various isomer cages. Despite of the fact that some of these fullerenes had tubular, ellipsoidal shapes, the current study seems to be the first application of the ZZ polynomial theory to tubular benzenoids, as the previously studied capped nanotubes formally belong to spherical benzenoids.

An interesting alternative to brute-force computation of ZZ polynomials using partial covering decomposition algorithms is the determination of closed formulas valid for the whole families of isostructural hydrocarbons indexed either by one, two, or three structural parameters n, m, and k. Various classes of catacondensed and pericondensed benzenoids have been treated that way, which resulted in the reported ZZ polynomials for polyacenes $L(n)$ [9, 92, 93], single armchair chains $N(n)$ [9, 34, 48, 49, 51], polyphenylenes $P(n)$ [9], multiple segment polyacenes [10, 12, 92, 93], cyclophenacenes [11, 24], hammers $H(n)$ [10], starphenes $St(n, m, k)$ [10], tripods $T(n, m, k)$ [10,13], zigzag coronoids $ZC(n, m, k)$ [10,12,15,24], fenestrenes $F(n, m)$ [10,12,15,24,43], parallelograms $M(m, n)$ [9,12,14,26,34], hexagons $O(n, m, k)$ [10, 13, 32, 89], chevrons $Ch(n, m, k)$ [10, 14], multiple zigzag chains $Z(n, m)$ [8, 10, 13, 34, 50, 88], ribbons $Rb(n, m, k)$ [10, 31], oblate rectangles $Or(n, m)$ [10, 13, 29, 32, 95], prolate rectangles $Pr(n, m)$ [10, 16, 92, 94], and many other benzenoids with more complex structure [9, 10, 13, 16, 30, 33, 34, 85, 92, 95].

ZZ polynomials stimulated many interesting mathematical associations, including the connections to sextet polynomials [1,2,27,37,92–94], to cube polynomials [6, 96], and to tiling polynomials [51]. The connection to cube polynomials allowed to investigate the distribution of zeros of ZZ polynomials [53]. An interesting direction of research in the theory of ZZ polynomials is related to expressing the ZZ polynomials as determinants of some structured sparse matrices [31–34, 88]. This bears a striking similarity to the celebrated John-Sachs theorem stating that the number of Kekulé structures of some benzenoid **B** can be compactly expressed as the determinant of the John-Sachs matrix $\mathbb{P}(\mathbf{B})$ [34, 35, 39]. The investigation of symmetries present in the ZZ polynomials of regular n-tier strips [86, 87] allowed to discover [45] an equivalence of ZZ polynomials to the extended strict order polynomials [44], demonstrating that the problem of enumeration of Clar covers for regular n-tier strip benzenoids is

equivalent to the problem of enumeration of linear extensions for partially ordered sets [46, 47]. Finally, various generalization of the ZZ polynomials has been reported, including various other cycles (C_4, C_8, C_{10}) as the covering components [20, 81, 98].

The current study relies on the recursive covering character assignment decomposition algorithm [9,12,29], the interface theory of benzenoids [31,42,43,48,49], and the transfer matrix technique [41,56,95] to construct and enumerate Clar covers for two classes of carbon nanotubes: zigzag and armchair nanotubes. Formal mathematical definition of these structures, usually obtained by folding appropriate patches of graphene sheet, is not discussed here; instead, we resort to implicit definitions given via the illustrations in Figs. 1 and 3 and we refer the interested readers to the abundant literature on the topic [18, 19, 55, 78, 79, 91].

3 Clar cover theory of zigzag nanotubes

Consider a zigzag nanotube $(n, 0)$ of length d. We denote it briefly here as $(n, 0)_d$. An example of such a nanotube is shown in Fig. 1a, and its planar representation in Fig. 1c. To construct a Clar cover $\mathbf{C}$ of $(n, 0)_d$, we consider an arbitrary edge ab located at the zigzag border $(n, 0)_d$ and assign to it single (S), double (D), or aromatic (A) covering character using the usual decomposition algorithm [1, 9, 92] used for constructing Clar covers. In the language of graph theory we say that

$$ab \text{ has character D} \iff \exists\, K_2 \in \mathbf{C} : ab \in E(K_2) \tag{7}$$

$$ab \text{ has character A} \iff \exists\, C_6 \in \mathbf{C} : ab \in E(C_6) \tag{8}$$

$$ab \text{ has character S} \iff ab \text{ is not covered in } \mathbf{C} \tag{9}$$

where $E(G)$ represents the set of edges of a graph G. This threefold way of assigning a definite covering character to ab, represented graphically in Fig. 2, has the following consequences:

- In case, when the edge ab is assigned the covering character S, the only way to construct a Clar cover proceeds via assigning character

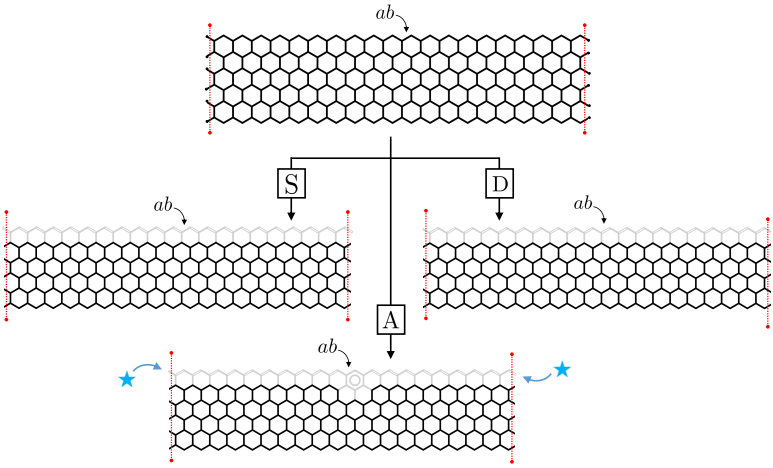
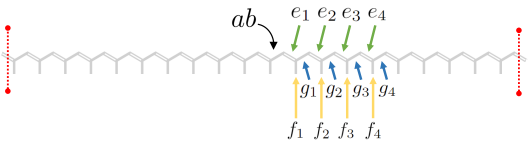


Figure 2. Threefold way of assigning a definite covering character S, D, or A to the edge ab located at the first layer of $(n,0)_d$ results in two distinct Kekulé-like coverings of the whole first zigzag layer in $(n,0)_d$; for details, see text. Note that assigning aromatic character (A) to the edge ab cannot produce any Clar cover, as one edge (denoted by asterisks) in the first layer of $(n,0)_d$ has simultaneously characters S and D, which is a contradiction.

D to the edge e_1 adjacent to ab to the right, which is turn mandates allocating single character S to the two next edges adjacent to e_1, i.e., the edge f_1 pointing down and the edge g_1 pointing to the right and parallel to ab. This patterns continues: The consecutive edges e_2, e_3, e_4, etc., are assigned character D, while single character S is assigned to the consecutive edges f_2, f_3, f_4, ..., (vertical edges) and the consecutive edges g_2, g_3, g_4, ..., (edges parallel to ab).



An extension of this pattern, after reaching the scission line and continuing through it, returns to the edge ab from the left side, as

shown on the diagram above. The resulting sequence of the coverings of the edges ab, e_1, g_1, e_2, g_2, e_3, g_3, e_4, etc., is purely Kekuléan ...SDSDSDSD..., with the S covering of the edge ab. Note that all the pointing down edges f_i are assigned the covering character S, which means that the covering of the next zigzag layer of $(n,0)_d$ is independent of the covering of the current zigzag layers, as zigzag layers of a zigzag nanotube are essentially disconnected from each other.

- In case, when the edge ab is assigned character D, the recursive assignment procedure described above is almost identical, but now one needs to proceed to the left instead to the right of the edge ab. The resulting sequence of the edge coverings is again purely Kekuléan ...DSDSDSDS..., with the D covering of the edge ab. (For details, see the branch $\boxed{\text{D}}$ in Fig. 2.) Again, all the pointing down edges f_i are assigned the covering character S, which means that the covering of the next zigzag layer of $(n,0)_d$ is independent of the covering of the current zigzag layers, as both layers are essentially disconnected.

- In case, when the edge ab is assigned the covering character A, the hexagon containing the edge ab is flanked on each side by alternating sequences of singly and doubly covered zigzag edges; the resulting sequence of the edge coverings is ...SDSDSAASDSDS... The edge crossed by the scission line is simultaneously assigned the covering character S (on the left side) and the covering character D (on the right side). (For details, see the two asterisks in the branch $\boxed{\text{A}}$ of Fig. 2.) This conflicting double assignment of the same edge is a clear contradiction, which shows that the assignment of A to the edge ab cannot produce any valid Clar cover of $(n,0)_d$.

In summary, an attempt to assign a definite covering character (S, D, or A) to an arbitrary edge ab located in the first zigzag layer of $(n,0)_d$ produces two distinct coverings of the first zigzag layer, both Kekuléan in their character and both consisting of an alternating sequences of n single and n double covering characters, S and D. These two coverings are distinct, as they differ by the covering character of the designated edge ab, which is

either S or D. Note, that in both cases all the vertical edges f_i, parallel to the axis of the nanotube, are assigned character S, stipulating that each zigzag layer of $(n,0)_d$ is essentially disconnected from other zigzag layers. Each zigzag layer of $(n,0)_d$ is covered in analogous way, always producing two distinct purely Kekuléan Clar coverings of this zigzag layer. Each consecutive zigzag layer is covered independently of the previous one and the next one. Consequently, the number of distinct Clar covers of $(n,0)_d$ is equal to 2^d; all these Clar covers are Kekuléan in their character. Note that this fact has been previously deduced by Zhang and Wang [91], who demonstrated that zigzag nanotubes are not 1-resonant, i.e., they do not permit any Clar sextet in their coverings. Consequently, the Zhang-Zhang polynomial of $(n,0)_d$ is given trivially by the following expression

$$ZZ\left((n,0)_d, x\right) = 2^d \tag{10}$$

4 Clar cover theory of armchair nanotubes

Consider an armchair nanotube (n,n) of length d. We will denote it briefly as $(n,n)_d$. An example of such a nanotube is shown in Fig. 1b, and its planar representation in Fig. 1d. To construct a Clar cover of $(n,n)_d$, we could follow the same procedure as above, but it turns out that the Clar theory of armchair nanotubes is much richer than the Clar theory of zigzag nanotubes and we need to approach the problem in a different manner.

First, we generalize the definition of armchair carbon nanotubes $(n,n)_d$ to integer and half-integer values of d. The graphical definition of both these families of the $(n,n)_d$ armchair nanotubes is shown in Fig. 3 for a few selected small values of d. We believe that it is straightforward for the reader to envision these structures for an arbitrary value of d. The generalization to an arbitrary value of n, considered a standard and well-established problem in the theory of nanotubes [18, 19, 79, 91], is not discussed here.

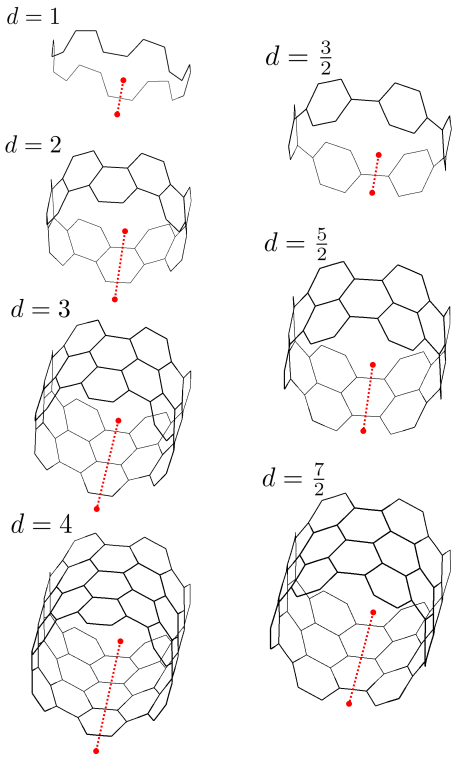


Figure 3. The length parameter d can assume integer or half-integer values for the armchair nanotubes $(n, n)_d$, generating two families of structures. Here, $n = 6$ and $d = 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \frac{7}{2}, 4$. The dotted lines symbolize a scission line allowing for representing $(n, n)_d$ as planar structures as shown in Fig. 4.

4.1 Fragments and their shapes

The tubular structures of nanotubes shown in Fig. 3 are somewhat cumbersome for further analysis. Therefore, in Fig. 4, we show planar representations of these structures allowing us to introduce later the transfer matrix technique. The transition from the tubular representation to the planar representation is straightforward: A scission of the tubular structures along the red dotted lines shown in Fig. 3 produces planar patches shown in Fig. 4. The scission line is repeated twice at the left and the right border of each planar patch. One should be aware that the pairs of the

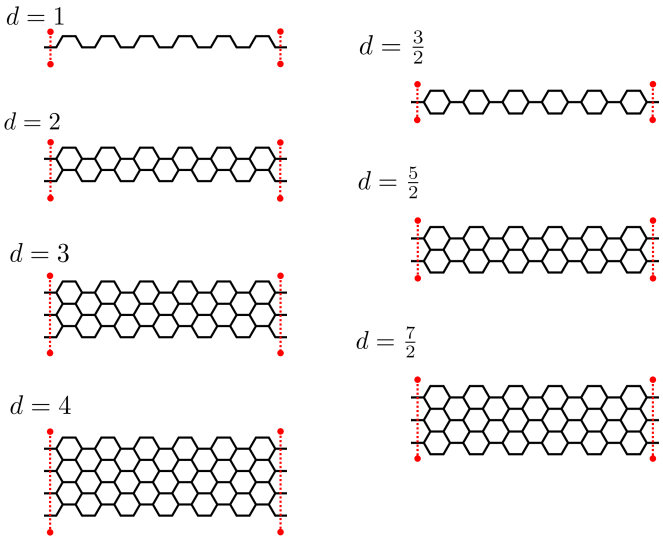


Figure 4. Planar representation of the armchair nanotubes $(n, n)_d$ shown in Fig. 3. The two copies of the dotted lines on both sides of each planar patch symbolize the scission lines from Fig. 3. The pairs of edges in the planar patches crossed by the scission lines are connected with each other.

corresponding horizontal edges crossed by the scission lines at both borders of the planar structures are repeated and should be always identified with each other.

In the next step needed to introduce the transfer matrix technique, the planar patches need to be divided further into smaller repeated fragments. This procedure is explained schematically in Fig. 5 on examples of four structures from Fig. 4 with $d = \frac{5}{2}, 3, \frac{7}{2}$ and 4. The dotted (blue) partition lines, parallel to the dotted (red) scission lines, divide the patches into smaller pieces referred to as fragments. For each value of d and n, only two distinct fragments are produced. For integer values of d, the fragments are abbreviated as ${}_d\mathtt{U}_d$ and ${}_d\mathtt{D}_d$, where `U` stands for 'up' and `D` stands for 'down'. For half-integer values of d, the fragments are abbreviated as ${}_{\lceil d \rceil}\mathtt{N}_{\lfloor d \rfloor}$ and ${}_{\lfloor d \rfloor}\mathtt{W}_{\lceil d \rceil}$, where `N` stands for 'narrow' and `W` stands for 'wide'. The subscripts denote the number of horizontal edges crossed by the partition lines of the left and right borders of each fragment; these sets

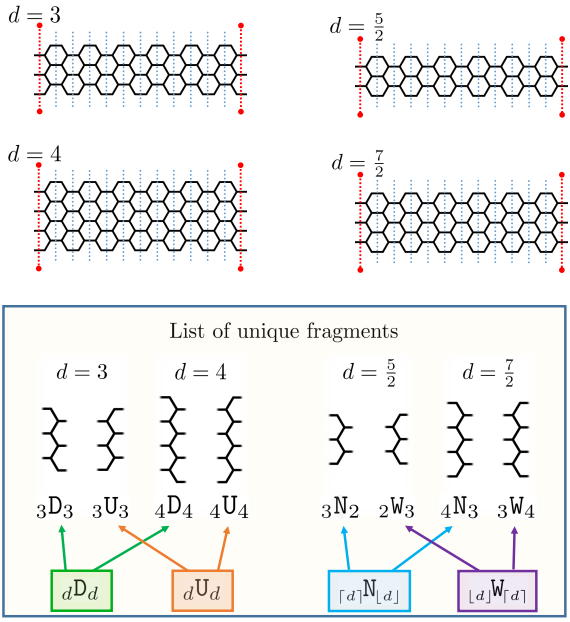


Figure 5. The planar representation of an armchair nanotube $(n,n)_d$ can be divided further into smaller fragments using dotted (blue) partition lines parallel to the dotted (red) scission lines. The resulting fragments, depending on their shape, are referred to as `D` (down), `U` (up), `N` (narrow), and `W` (wide).

of edges will be referred to in the following as the left and right interfaces, respectively, of each fragment. Analogously, the left and right subscripts in ${}_d\mathtt{U}_d$, ${}_d\mathtt{D}_d$, ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$, and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$ will be referred to as the lengths of the interfaces in each fragment. Note that every armchair nanotube $(n,n)_d$ can be unambiguously represented as a cyclic sequence of $2n$ fragments

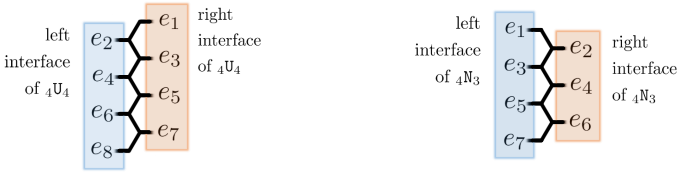
$$(n,n)_d = \begin{cases} (\underbrace{{}_d\mathtt{U}_d, {}_d\mathtt{D}_d, \ldots, {}_d\mathtt{U}_d, {}_d\mathtt{D}_d}_{2n}) & \text{for integer } d \\ (\underbrace{{}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}, {}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}, \ldots, {}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}, {}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}}_{2n}) & \text{for half-integer } d \end{cases} \tag{11}$$

We show in the following that Clar covers of $(n,n)_d$ can be conveniently constructed from coverings of the fragments ${}_d\mathtt{U}_d$, ${}_d\mathtt{D}_d$, ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$, and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$.

4.2 Interface theory of benzenoids

A detailed discussion of fragments and fragment coverings, with coherent definitions of these quantities and a rigorous discussion of their properties, was presented before as the interface theory of benzenoids [42, 43]. The exposition was quite lengthy, therefore we do not repeat it here and the reader is referred to the original paper. All the definitions, lemmas, and theorems of the interface theory of benzenoids [42] can be applied directly to the nanotube fragments introduced in the previous Section. The reader should be aware that the fragments `U` and `D` appeared as `R` and `L` in the original formulation [42], due to a different orientation of the fragments. Similarly, for the same reason, the upper and lower interfaces from [42] appear here as the left and right interfaces.

Let us briefly summarize the most important tenets of the interface theory of benzenoids, adapted here to the fragments of armchair nanotubes. Each fragment `F` possesses two interfaces, left $|\mathtt{F}\rangle$ and right $\langle\mathtt{F}|$, consisting



of all horizontal edges of the fragment, labelled as e_i from top to bottom. In this way, the left interface of $_4\mathtt{U}_4$, denoted as $|_4\mathtt{U}_4\rangle = |e_2, e_4, e_6, e_8\rangle$, and the right interface of $_4\mathtt{U}_4$, denoted as $\langle_4\mathtt{U}_4| = \langle e_1, e_3, e_5, e_7|$, both consist of four edges. Similarly, for $_4\mathtt{N}_3$, the interfaces (of length 4 and 3, respectively) are given by $|_4\mathtt{N}_3\rangle = |e_1, e_3, e_5, e_7\rangle$ and $\langle_4\mathtt{N}_3| = \langle e_2, e_4, e_6|$. In addition to the $d_1 + d_2$ interface edges $e_1, e_2, \ldots, e_{d_1+d_2}$, a fragment $_{d_1}\mathtt{F}_{d_2}$ contains also d_1+d_2-1 spine edges $s_1, s_2, \ldots, s_{d_1+d_2-1}$ and d_1+d_2 vertices (*aka* atoms) $v_1, v_2, \ldots, v_{d_1+d_2}$, numbered from top to bottom.

Each of the edges $g \in \{e_1, \ldots, e_{d_1+d_2}, s_1, \ldots, s_{d_1+d_2-1}\}$ of $_{d_1}\mathtt{F}_{d_2}$ can be assigned a definite covering character: single (S), double (D), or aromatic (A). We associate with each of these covering types a definite edge order

(*aka* bond order)

$$\operatorname{ord}(g) = \begin{cases} 1 & \text{if } g \text{ has covering type D} \\ 1/2 & \text{if } g \text{ has covering type A} \\ 0 & \text{if } g \text{ has covering type S} \end{cases} \tag{12}$$

It is convenient to define edge covering function; we have

$$\operatorname{cov}(g) = \begin{cases} \mathrm{D} & \text{if } \operatorname{ord}(g) = 1 \\ \mathrm{A} & \text{if } \operatorname{ord}(g) = 1/2 \\ \mathrm{S} & \text{if } \operatorname{ord}(g) = 0 \end{cases} \tag{13}$$

The notion of covering order can be immediately extended to vertices

$$\operatorname{ord}(v_j) = \operatorname{ord}(s_{j-1}) + \operatorname{ord}(e_j) + \operatorname{ord}(s_j) \tag{14}$$

where we set $\operatorname{ord}(s_{-1}) = \operatorname{ord}(s_{d_1+d_2}) \equiv 0$, and to interfaces

$$\operatorname{ord}(i) = \operatorname{ord}(e_{j_1}) + \operatorname{ord}(e_{j_2}) + \cdots + \operatorname{ord}(e_{j_d}) \tag{15}$$

where $i = |\mathtt{F}\rangle = |e_{j_1}, e_{j_2}, \ldots, e_{j_d}\rangle$ or $i = \langle \mathtt{F}| = \langle e_{j_1}, e_{j_2}, \ldots, e_{j_d}|$ is an interface of length d. Similarly, the value of the interface covering function cov is defined as a d-letter word

$$\operatorname{cov}(i) = \operatorname{cov}(e_{j_1}) \operatorname{cov}(e_{j_2}) \operatorname{cov}(e_{j_3}) \cdots \operatorname{cov}(e_{j_d}) \tag{16}$$

obtained by concatenating covering characters of consecutive interface edges $e_{j_1}, e_{j_2}, \ldots, e_{j_d}$. The interface $i = |\mathtt{F}\rangle$ together with its covering will be denoted as $|\operatorname{cov}(i)\rangle$ and the interface $i = \langle \mathtt{F}|$ together with its covering will be denoted as $\langle \operatorname{cov}(i)|$.

Obviously, not every covering character assignment described above results in a valid covering of a fragment that can be used for constructing Clar covers. (For example, assigning the covering character A to e_j necessarily implies that either

$$\operatorname{ord}(s_j) = \operatorname{ord}(s_{j+1}) = \operatorname{ord}(e_{j+2}) = 1/2 \quad \text{and} \quad \operatorname{ord}(e_{j+1}) = 0$$

or

$$\mathrm{ord}\,(s_j - 1) = \mathrm{ord}\,(s_{j-2}) = \mathrm{ord}\,(e_{j-2}) = 1/2 \quad \text{and} \quad \mathrm{ord}\,(e_{j-1}) = 0$$

All assignments that do not comply with one of these requirements cannot possibly constitute a valid fragment covering, as they do not satisfy Eq. (8).) Sufficient and necessary conditions for a covering of $\mathtt{F}$ to be valid have been given in [42] as the three rules of the interface theory of benzenoids. We reproduce them here (without proofs) adapted to the current discussion. Theorems 1 and 2 give necessary conditions that need to be satisfied by the covering characters of interface edges of each fragment within a given Clar cover **C**. Theorem 3 gives a sufficient condition for a collection of covering characters of all interface edges in $(n,n)_d$ to define a Clar cover of $(n,n)_d$. Later, Theorem 3 is reformulated as a practical recipe for constructing all Clar covers of $(n,n)_d$.

Theorem 1 (First rule of interface theory, Theorem 11 of [42])**.** *Let* **C** *be a Clar cover of* $(n,n)_d$*. Let* $\mathtt{F}$ *be a fragment of* $(n,n)_d$*, with covering characters decided by* **C***, and let* $|\mathtt{F}\rangle$ *and* $\langle\mathtt{F}|$ *be the left and right interfaces of* $\mathtt{F}$*, respectively. The following conditions are always satisfied:*

(*a*) *If* $\mathtt{F} = {}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$*, then* $\mathrm{ord}\,(\langle\mathtt{F}|) = \mathrm{ord}\,(|\mathtt{F}\rangle) + 1$.

(*b*) *If* $\mathtt{F} = {}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$*, then* $\mathrm{ord}\,(\langle\mathtt{F}|) = \mathrm{ord}\,(|\mathtt{F}\rangle) - 1$.

(*c*) *If* $\mathtt{F} = {}_d\mathtt{U}_d$ *or* $\mathtt{F} = {}_d\mathtt{D}_d$*, then* $\mathrm{ord}\,(\langle\mathtt{F}|) = \mathrm{ord}\,(|\mathtt{F}\rangle)$.

Theorem 2 (Second rule of interface theory, Theorem 16 of [42])**.** *Let* **C** *be a Clar cover of* $(n,n)_d$*. Let* ${}_{d_1}\mathtt{F}_{d_2}$ *be a fragment of* $(n,n)_d$ *with covering characters decided by* **C***. The covering characters* D *and* A *are distributed over* $|{}_{d_1}\mathtt{F}_{d_2}\rangle$ *and* $\langle{}_{d_1}\mathtt{F}_{d_2}|$ *as follows:*

(*a*) *The first occurrence of* D *or* A *in the interface edges* $e_1, e_2, \ldots, e_{d_1+d_2}$ *happens for* e_j *with an odd value of* j*.*

(*b*) *The last occurrence of* D *or* A *in the interface edges* $e_1, e_2, \ldots, e_{d_1+d_2}$ *happens for* e_j *with an odd value of* $d_1 + d_2 - j$*.*

(c) *If* e_j *and* $e_{j'}$ *(with* $j' > j$*) are two consecutive interface edges with covering characters* A *or* D *(i.e.,* $\mathrm{ord}\,(e_k) = 0$ *for* $j < k < j'$*), then either:*

(c') $j' - j$ *is odd, which signifies that one of the pair* $(e_j, e_{j'})$ *is in* $|_{d_1}\mathrm{F}_{d_2}\rangle$*, and the other one in* $\langle_{d_1}\mathrm{F}_{d_2}|$*,*

or

(c") $j' - j = 2$*, which signifies that both* e_j *and* $e_{j'}$ *are located in the same interface,* $|_{d_1}\mathrm{F}_{d_2}\rangle$ *or* $\langle_{d_1}\mathrm{F}_{d_2}|$*, being a part of the same aromatic sextet* C_6*,* $e_j, e_{j'} \in E\,(C_6)$ *.*

NOTE *The condition* (c") *implies that* $\mathrm{ord}\,(e_j) = \mathrm{ord}\,(e_{j'}) = 1/2$*, and also that* $\mathrm{ord}\,(s_j) = \mathrm{ord}\,(s_{j+1}) = 1/2$*.*

Theorem 3 (Third rule of interface theory, Theorem 21 of [42])**.** *Let us assume that the covering characters* S, D, *and* A *have been assigned to all interface edges in* $(n, n)_d$ *in such a way that:*

(a) *The set of edges with the covering character* A *can be written as a union of disjoint pairs* (e_j, e_{j+2})*. Moreover, for each pair* (e_j, e_{j+2})*, the condition* $\mathrm{ord}\,(e_{j+1}) = 0$ *is also satisfied.*

(b) *The orders of all interfaces in* $(n, n)_d$ *satisfy the conditions* (a)*,* (b)*, and* (c) *of Theorem 1.*

(c) *The orders of all interface edges in* $(n, n)_d$ *satisfy the conditions* (a) *and* (b) *of Theorem 2.*

(d) *If* e_j *and* $e_{j'}$ *(with* $j' > j$*) are two consecutive interface edges with covering characters* A *or* D *(for details, see the condition* (c) *of Theorem 2), then either:*

(d') $j' - j$ *is odd,*

or

(d") $j' - j = 2$ *and* $(e_j, e_{j'})$ *is one of the pairs of edges with covering characters* A *specified in the condition* (a) *of Theorem 3.*

Then, there is exactly one Clar cover $\mathbf{C}$ *of* $(n,n)_d$ *with the specified collection of covering characters of interface edges.*

Theorem 3 shows that all Clar covers of $(n,n)_d$ can be generated by considering all possible covering assignments of the interface edges in $(n,n)_d$, which satisfy the conditions (a), (b), (c), and (d) of Theorem 3. Lemma 5 of [42] shows that for every Clar cover $\mathbf{C}$ (i.e., for a spanning subgraph of $(n,n)_d$), every vertex (atom) v in $(n,n)_d$ has order one, $\mathrm{ord}\,(v) = 1$, independently of the choice of $\mathbf{C}$. Similarly, Lemma 8 of [42] shows that the covering characters of interface edges in a Clar cover $\mathbf{C}$ uniquely define the orders (and hence: covering characters) of all the spine edges in $(n,n)_d$. In other words, in order to generate all Clar covers of $(n,n)_d$, we need to concern ourselves here only with all possible choice of the covering characters for the interface edges in $(n,n)_d$, as all other components of each $\mathbf{C}$ can be determined from these quantities.

The conditions (a), (b), (c), and (d) of Theorem 3 have local characters, i.e., they are always concerning either one interface (located between two consecutive fragments) or one fragment (located between two consecutive interfaces) of $(n,n)_d$. The following obvious Lemma simplifies this situation and focuses our attention solely on single fragments of $(n,n)_d$.

Lemma 4. *Let* $\mathtt{F}_1$ *and* $\mathtt{F}_2$ *be two consecutive fragments of* $(n,n)_d$ *such that the right interface* $i_1 = \langle \mathtt{F}_1|$ *of* $\mathtt{F}_1$ *is identical with the left interface* $i_2 = |\mathtt{F}_2\rangle$ *of* $\mathtt{F}_2$*. Then the covering characters of both interfaces induced by* $\mathbf{C}$ *are identical*

$$\mathrm{cov}\,(i_1) = \mathrm{cov}\,(i_2)$$

This Lemma has quite far-reaching consequences: it is sufficient to construct all the possible valid coverings of unique fragments of $(n,n)_d$ by assigning covering characters to both interfaces of each fragment in agreement with conditions (a), (b), (c), and (d) of Theorem 3. Fragment coverings constructed in this way can be subsequently used to construct Clar covers of $(n,n)_d$ by connecting them like jig-saw puzzles in the way stipulated by Lemma 4. We show below that an efficient tool for performing this operation is provided by the transfer matrix methodology.

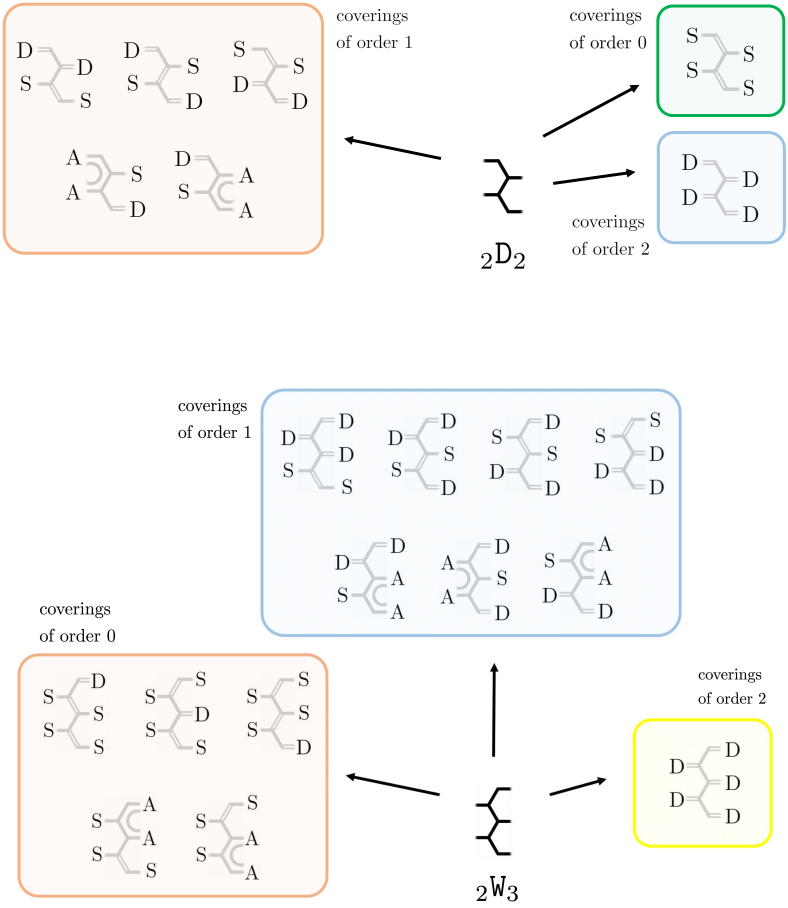


Figure 6. There are 7 distinct coverings of the fragment $_2\mathtt{D}_2$ and 13 distinct coverings of the fragment $_2\mathtt{W}_3$ constructed in agreement with conditions (a), (b), (c), and (d) of Theorem 3. The coverings can be grouped together into classes with identical orders of the fragment's interfaces. (For details, see text.) Each covering can be uniquely and conveniently represented by specifying the covering characters of the fragment's left and right interfaces (e.g., $|\mathrm{AA}\rangle\langle\mathrm{SD}|$ or $|\mathrm{DD}\rangle\langle\mathrm{DD}|$ for the fragment $_2\mathtt{D}_2$, and $|\mathrm{DS}\rangle\langle\mathrm{DAA}|$ or $|\mathrm{AA}\rangle\langle\mathrm{DSD}|$ for the fragment $_2\mathtt{W}_3$). Note that the coverings of the fragment $_2\mathtt{U}_2$ are mirror images of those for $_2\mathtt{D}_2$, and the coverings of the fragment $_3\mathtt{N}_2$ are mirror images of those for $_2\mathtt{W}_3$.

4.3 Fragment coverings

Consider a fragment F having one of the following shapes: ${}_{d}\mathtt{U}_{d}$, ${}_{d}\mathtt{D}_{d}$, ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$, or ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$. Each of the interface edges of F can be assigned a definite covering character: single (S), double (D), or aromatic (A), in agreement with the conditions (a), (b), (c), and (d) of Theorem 3. Lemmas 5 and 8 of [42] stipulate that the covering characters of remaining (spine) edges of F are uniquely defined by the specification of the covering character of the interface edges of F. Fig. 6 gives an example of all the possible coverings that can be constructed for the fragments ${}_{2}\mathtt{D}_{2}$ and ${}_{2}\mathtt{W}_{3}$; there are 7 coverings for ${}_{2}\mathtt{D}_{2}$ and 13 coverings for ${}_{2}\mathtt{W}_{3}$. Note that since the fragments ${}_{2}\mathtt{U}_{2}$ and ${}_{3}\mathtt{N}_{2}$ are mirror images of ${}_{2}\mathtt{D}_{2}$ and ${}_{2}\mathtt{W}_{3}$, respectively, the mirror image of Fig. 6 effectively shows also all the possible coverings of ${}_{2}\mathtt{U}_{2}$ and ${}_{3}\mathtt{N}_{2}$; this mirror image symmetry immediately generalizes to the ${}_{d}\mathtt{D}_{d} \leftrightarrow {}_{d}\mathtt{U}_{d}$ and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil} \leftrightarrow {}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$ pairs.

A covering of F can be conveniently referred to by providing two strings of covering characters for the edges in the left and right interfaces of F. For example, any covering of ${}_{2}\mathtt{D}_{2}$ is given by the symbol

$$\mathrm{cov}\,({}_{2}\mathtt{D}_{2}) = \Big|\,\mathrm{cov}(e_1)\ \mathrm{cov}(e_3)\Big\rangle\Big\langle\mathrm{cov}(e_2)\ \mathrm{cov}(e_4)\,\Big|$$

while a covering of ${}_{2}\mathtt{W}_{3}$ is given by the symbol

$$\mathrm{cov}\,({}_{2}\mathtt{W}_{3}) = \Big|\,\mathrm{cov}(e_2)\ \mathrm{cov}(e_4)\,\Big\rangle\Big\langle\mathrm{cov}(e_1)\ \mathrm{cov}(e_3)\ \mathrm{cov}(e_5)\,\Big|$$

The notion of fragment covering can be immediately generalized to an arbitrary fragment ${}_{d}\mathtt{D}_{d}$ and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$; we have

$$\mathrm{cov}\,({}_{d}\mathtt{D}_{d}) = \Big|\,\mathrm{cov}(e_1)\cdots\mathrm{cov}(e_{2d-1})\Big\rangle\Big\langle\mathrm{cov}(e_2)\cdots\mathrm{cov}(e_{2d})\,\Big| \quad (17)$$

$$\mathrm{cov}\,\big({}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}\big) = \Big|\,\mathrm{cov}(e_2)\cdots\mathrm{cov}(e_{2d-1})\Big\rangle\Big\langle\mathrm{cov}(e_1)\cdots\mathrm{cov}(e_{2d})\,\Big| \quad (18)$$

The Dirac bra-ket notation, borrowed from physics and adapted here for the alphanumeric representation of interface coverings, has several advantages. For example, the mirror symmetry ${}_{d}\mathtt{D}_{d} \leftrightarrow {}_{d}\mathtt{U}_{d}$ and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil} \leftrightarrow {}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$ is readily expressed in this notation by the usual "Hermitian conjugation"

operation; we have

$$\begin{aligned}\operatorname{cov}\left({}_{d}\mathtt{U}_{d}\right) &= \operatorname{cov}\left({}_{d}\mathtt{D}_{d}\right)^{\dagger} \\ &= \Big|\operatorname{cov}(e_2)\cdots\operatorname{cov}(e_{2d})\Big\rangle\Big\langle\operatorname{cov}(e_1)\cdots\operatorname{cov}(e_{2d-1})\Big| \quad (19)\\ \operatorname{cov}\left({}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}\right) &= \operatorname{cov}\left({}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}\right)^{\dagger} \\ &= \Big|\operatorname{cov}(e_1)\cdots\operatorname{cov}(e_{2d})\Big\rangle\Big\langle\operatorname{cov}(e_2)\cdots\operatorname{cov}(e_{2d-1})\Big| \quad (20)\end{aligned}$$

Other advantages will be discussed later in connection with the transfer matrices.

Denoting by $\operatorname{covs}(\mathtt{F})$ the set of all coverings of the fragment $\mathtt{F}$, we see immediately from Fig. 6 that

$$\begin{aligned}\operatorname{covs}\left({}_{2}\mathtt{D}_{2}\right) &= \big\{\big|\mathrm{DD}\big\rangle\big\langle\mathrm{DD}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{DS}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{SD}\big|, \big|\mathrm{SD}\big\rangle\big\langle\mathrm{SD}\big|, \\ &\quad \big|\mathrm{AA}\big\rangle\big\langle\mathrm{SD}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{AA}\big|, \big|\mathrm{SS}\big\rangle\big\langle\mathrm{SS}\big|\big\} \quad (21)\\ \operatorname{covs}\left({}_{2}\mathtt{W}_{3}\right) &= \big\{\big|\mathrm{DD}\big\rangle\big\langle\mathrm{DDD}\big|, \big|\mathrm{SD}\big\rangle\big\langle\mathrm{SDD}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{DAA}\big|, \big|\mathrm{AA}\big\rangle\big\langle\mathrm{DSD}\big|, \\ &\quad \big|\mathrm{SD}\big\rangle\big\langle\mathrm{AAD}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{DDS}\big|, \big|\mathrm{DS}\big\rangle\big\langle\mathrm{DSD}\big|, \big|\mathrm{SD}\big\rangle\big\langle\mathrm{DSD}\big|, \\ &\quad \big|\mathrm{SS}\big\rangle\big\langle\mathrm{DSS}\big|, \big|\mathrm{SS}\big\rangle\big\langle\mathrm{SDS}\big|, \big|\mathrm{SS}\big\rangle\big\langle\mathrm{SSD}\big|, \big|\mathrm{SS}\big\rangle\big\langle\mathrm{AAS}\big|, \\ &\quad \big|\mathrm{SS}\big\rangle\big\langle\mathrm{SAA}\big|\big\} \quad (22)\end{aligned}$$

The mirror symmetry ${}_{d}\mathtt{D}_{d} \leftrightarrow {}_{d}\mathtt{U}_{d}$ and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil} \leftrightarrow {}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$, expressed via the conjugation operation $(\,)^{\dagger}$ introduced above, leads immediately to the following general expressions

$$\begin{aligned}\operatorname{covs}\left({}_{d}\mathtt{U}_{d}\right) &= \left\{c^{\dagger} \mid c \in \operatorname{covs}\left({}_{d}\mathtt{D}_{d}\right)\right\} \quad (23)\\ \operatorname{covs}\left({}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}\right) &= \left\{c^{\dagger} \mid c \in \operatorname{covs}\left({}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}\right)\right\} \quad (24)\end{aligned}$$

which specialize for $d = 2$ and $d = {}^5\!/_2$, respectively, to

$$\begin{aligned}\mathrm{covs}\,({}_2\mathtt{U}_2) \;=\; & \big\{\big|\mathrm{DD}\big\rangle\big\langle\mathrm{DD}\big|\,,\big|\mathrm{DS}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{SD}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{SD}\big\rangle\big\langle\mathrm{SD}\big|\,,\\ & \big|\mathrm{AA}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{SD}\big\rangle\big\langle\mathrm{AA}\big|\,,\big|\mathrm{SS}\big\rangle\big\langle\mathrm{SS}\big|\big\} \qquad (25)\\ \mathrm{covs}\,({}_3\mathtt{N}_2) \;=\; & \big\{\big|\mathrm{DDD}\big\rangle\big\langle\mathrm{DD}\big|\,,\big|\mathrm{SDD}\big\rangle\big\langle\mathrm{SD}\big|\,,\big|\mathrm{DAA}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{DSD}\big\rangle\big\langle\mathrm{AA}\big|\,,\\ & \big|\mathrm{AAD}\big\rangle\big\langle\mathrm{SD}\big|\,,\big|\mathrm{DDS}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{DSD}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{DSD}\big\rangle\big\langle\mathrm{SD}\big|\,,\\ & \big|\mathrm{DSS}\big\rangle\big\langle\mathrm{SS}\big|\,,\big|\mathrm{SDS}\big\rangle\big\langle\mathrm{SS}\big|\,,\big|\mathrm{SSD}\big\rangle\big\langle\mathrm{SS}\big|\,,\big|\mathrm{AAS}\big\rangle\big\langle\mathrm{SS}\big|\,,\\ & \big|\mathrm{SAA}\big\rangle\big\langle\mathrm{SS}\big|\big\} \qquad (26)\end{aligned}$$

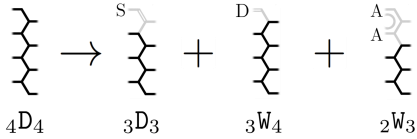
Note that Eqs. (23) and (24) allow us to focus only on the coverings of fragments ${}_d\mathtt{D}_d$ and ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$, because the corresponding expressions for $\mathrm{covs}\,({}_d\mathtt{U}_d)$ and $\mathrm{covs}\,\big({}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}\big)$ can be always obtained from Eqs. (23) and (24). In the next section, we show that $\mathrm{covs}\,({}_d\mathtt{D}_d)$ and $\mathrm{covs}\,\big({}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}\big)$ can be easily constructed using certain recurrence relations.

4.4 Recurrence relations for coverings of fragments

All coverings of the fragments ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$, ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$, ${}_d\mathtt{U}_d$, and ${}_d\mathtt{D}_d$ can be constructed recursively in the up-to-down manner by assigning a single (S), a double (D), or an aromatic (A) character to the top interface edge in a given fragment. This operation results in a partially covered fragment, where the not-yet-covered part has again one of the possible fragment shapes (N, W, U, and D), but with shorter left and/or right interfaces. For $k \geq 3$, the following recurrence relations can be inferred

$$\begin{aligned}{}_k\mathtt{N}_{k-1} \;&\to\; {}_{k-1}\mathtt{N}_{k-2} + {}_{k-1}\mathtt{U}_{k-1} + {}_{k-2}\mathtt{U}_{k-2} && (27)\\ {}_k\mathtt{W}_{k+1} \;&\to\; {}_{k-1}\mathtt{W}_{k} + {}_{k}\mathtt{D}_{k} + {}_{k-1}\mathtt{D}_{k-1} && (28)\\ {}_k\mathtt{U}_{k} \;&\to\; {}_{k-1}\mathtt{U}_{k-1} + {}_{k}\mathtt{N}_{k-1} + {}_{k-1}\mathtt{N}_{k-2} && (29)\\ {}_k\mathtt{D}_{k} \;&\to\; \underbrace{{}_{k-1}\mathtt{D}_{k-1}}_{\mathrm{S}} + \underbrace{{}_{k-1}\mathtt{W}_{k}}_{\mathrm{D}} + \underbrace{{}_{k-2}\mathtt{W}_{k-1}}_{\mathrm{A}} && (30)\end{aligned}$$

where the letter under the brace indicates which covering character has been used in the current recursive assignment step. A graphical proof



(31)

of one of these relations suggests how to derive the remaining formulas. Consecutive application of the recurrence relations (27)–(30) until all the interface edges of a given fragment has been assigned a definite character produces all possible coverings of each fragment. Note that the recurrence relations (27)–(30) are not applicable to fragments with small values of k; coverings of these fragments need to be treated separately. The coverings for $_2\mathtt{D}_2$, $_3\mathtt{N}_2$, $_2\mathtt{U}_2$, and $_2\mathtt{W}_3$ have been given by Eqs. (21), (22), (25), and (26), respectively. The remaining sets are readily constructed:

$$\operatorname{covs}(_1\mathtt{U}_1) \;=\; \operatorname{covs}(_1\mathtt{D}_1) \;=\; \big\{\big|\mathrm{D}\big\rangle\big\langle\mathrm{D}\big|\,,\big|\mathrm{S}\big\rangle\big\langle\mathrm{S}\big|\big\} \tag{32}$$

$$\operatorname{covs}(_2\mathtt{N}_1) \;=\; \big\{\big|\mathrm{DD}\big\rangle\big\langle\mathrm{D}\big|\,,\big|\mathrm{DS}\big\rangle\big\langle\mathrm{S}\big|\,,\big|\mathrm{AA}\big\rangle\big\langle\mathrm{S}\big|\,,\big|\mathrm{SD}\big\rangle\big\langle\mathrm{S}\big|\big\} \tag{33}$$

$$\operatorname{covs}(_1\mathtt{W}_2) \;=\; \big\{\big|\mathrm{D}\big\rangle\big\langle\mathrm{DD}\big|\,,\big|\mathrm{S}\big\rangle\big\langle\mathrm{DS}\big|\,,\big|\mathrm{S}\big\rangle\big\langle\mathrm{AA}\big|\,,\big|\mathrm{S}\big\rangle\big\langle\mathrm{SD}\big|\big\} \tag{34}$$

The number of coverings for the fragments $_k\mathtt{D}_k$ and $_k\mathtt{U}_k$ with $k \equiv d = 0, 1, 2, 3, \ldots$ forms the sequence $(1, 2, 7, 24, 81, 274, \ldots)$, identical (up to an offset) with the sequence A099463 in OEIS [73]. (To allow for this identification, we have implicitly assumed that for empty interfaces $_0\mathtt{U}_0$ and $_0\mathtt{D}_0$, we have $\big|\operatorname{covs}(_0\mathtt{U}_0)\big| = \big|\operatorname{covs}(_0\mathtt{D}_0)\big| = \big|\big\{\big|\;\big\rangle\big\langle\;\big|\big\}\big| = 1$.) Similarly, the number of coverings for the fragments $_k\mathtt{W}_{k+1}$ and $_{k+1}\mathtt{N}_k$ with $k \equiv \lfloor d \rfloor = 0, 1, 2, 3, \ldots$ forms the sequence $(1, 4, 13, 44, 149, 504, \ldots)$, identical (up to an offset) with the sequence A073717 in OEIS [72]. (Again, we have implicitly assumed that for the partially empty interfaces $_0\mathtt{W}_1$ and $_1\mathtt{N}_0$, we have $\big|\operatorname{covs}(_1\mathtt{N}_0)\big| = \big|\big\{\big|\mathrm{D}\big\rangle\big\langle\;\big|\big\}\big| = 1$ and $\big|\operatorname{covs}(_0\mathtt{W}_1)\big| = \big|\big\{\big|\;\big\rangle\big\langle\mathrm{D}\big|\big\}\big| = 1$.)

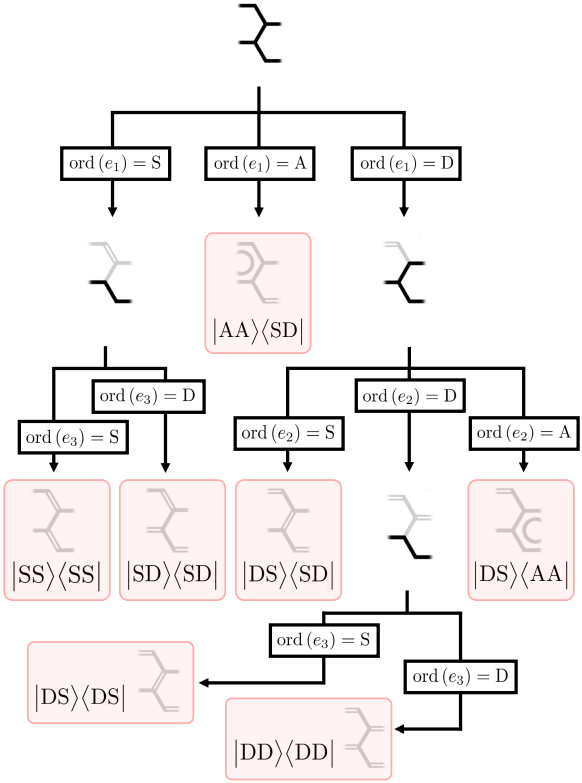


Figure 7. An algorithm based on consecutive application of the recurrence relations (27)–(30) to the fragment ${}_2\mathtt{D}_2$ until all its interface edges has been assigned a definite covering character produces all possible coverings of ${}_2\mathtt{D}_2$. The coverings of ${}_2\mathtt{D}_2$, shown in shadowed frames, are identical to those shown in the upper panel of Fig. 6, and to those listed in Eq. (21).

The generating functions for these sequences are

$$\left.\begin{array}{rcl} G_{\mathtt{D}}(t) & = & \displaystyle\sum_{k=0}^{\infty} \left|\operatorname{covs}\left({}_k\mathtt{D}_k\right)\right| t^k \\ G_{\mathtt{U}}(t) & = & \displaystyle\sum_{k=0}^{\infty} \left|\operatorname{covs}\left({}_k\mathtt{U}_k\right)\right| t^k \end{array}\right\} = \frac{1-t}{1-3t-t^2-t^3} \tag{35}$$

$$\left.\begin{array}{rcl} G_{\mathtt{N}}(t) & = & \displaystyle\sum_{k=0}^{\infty} \left|\operatorname{covs}\left({}_{k+1}\mathtt{N}_k\right)\right| t^k \\ G_{\mathtt{W}}(t) & = & \displaystyle\sum_{k=0}^{\infty} \left|\operatorname{covs}\left({}_k\mathtt{W}_{k+1}\right)\right| t^k \end{array}\right\} = \frac{1+t}{1-3t-t^2-t^3} \tag{36}$$

Expansions of these functions in t and rearrangements of the resulting sums produces closed-form formulas for the number of coverings of the analyzed fragments

$$\left.\begin{array}{l} \left|\operatorname{covs}\left({}_k\mathtt{D}_k\right)\right| \\ \left|\operatorname{covs}\left({}_k\mathtt{U}_k\right)\right| \end{array}\right\} = \sum_{i=0}^{\lfloor \frac{k}{3} \rfloor} \sum_{j=0}^{\lfloor \frac{k-3i}{2} \rfloor} \left(4 - \tfrac{i+j}{k-2i-j}\right) \binom{k-2i-j}{i+j} \binom{i+j}{j} 3^{k-1-2j-3i} \tag{37}$$

$$\left.\begin{array}{l} \left|\operatorname{covs}\left({}_{k+1}\mathtt{N}_k\right)\right| \\ \left|\operatorname{covs}\left({}_k\mathtt{W}_{k+1}\right)\right| \end{array}\right\} = \sum_{i=0}^{\lfloor \frac{k}{3} \rfloor} \sum_{j=0}^{\lfloor \frac{k-3i}{2} \rfloor} \left(2 + \tfrac{i+j}{k-2i-j}\right) \binom{k-2i-j}{i+j} \binom{i+j}{j} 3^{k-1-2j-3i} \tag{38}$$

These formulas are too complicated to be interpreted combinatorically. A slightly less complicated formula can be derived by the following observation. The sequence $\left(0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots\right)$, formed from all possible values of d, corresponds to the sequence $(1, 1, 2, 4, 7, 13, 24, 44, 81, \ldots)$, which can be generated by interleaving the sequences $\left(\left|\operatorname{covs}\left({}_k\mathtt{D}_k\right)\right|\right)$ and $\left(\left|\operatorname{covs}\left({}_k\mathtt{W}_{k+1}\right)\right|\right)$, and which is identical (up to offset) with the sequence A000073 in OEIS [69]. A000073 is a sequence of tribonacci numbers generated by the recurrence $a_n = a_{n-1} + a_{n-2} + a_{n-3}$ and initial conditions $a_0 = a_1 = 0$ and $a_2 = 1$. The generating function for this sequence (with the offset adjusted to our case) is given by $\left(1 - t - t^2 - t^3\right)^{-1}$, which after expansion gives the following general expression for the cardinalities of the fragment covering

sets:

$$\left.\begin{matrix} \left|\operatorname{covs}\left({}_{d}\mathtt{D}_{d}\right)\right| \\ \left|\operatorname{covs}\left({}_{d}\mathtt{U}_{d}\right)\right| \\ \left|\operatorname{covs}\left({}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}\right)\right| \\ \left|\operatorname{covs}\left({}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}\right)\right| \end{matrix}\right\} = \sum_{i=0}^{\lfloor \frac{2d}{3}\rfloor}\sum_{j=0}^{\lfloor d-\frac{3i}{2}\rfloor}\binom{2d-2i-j}{i+j}\binom{i+j}{j} \tag{39}$$

where one should remember that armchair nanotubes $(n,n)_d$ with integer values of d contain only fragments ${}_{d}\mathtt{U}_{d}$ and ${}_{d}\mathtt{D}_{d}$, while $(n,n)_d$ with half-integer values of d contain only fragments ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$ and ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$.

4.5 Fragment coverings as transfer matrices

There exists a much simpler and more transparent representation of the fragment coverings for ${}_{d}\mathtt{U}_{d}$, ${}_{d}\mathtt{D}_{d}$, ${}_{\lfloor d\rfloor}\mathtt{W}_{\lceil d\rceil}$, and ${}_{\lceil d\rceil}\mathtt{N}_{\lfloor d\rfloor}$. This representation is introduced most conveniently on an example. Let us consider again the set $\operatorname{covs}\left({}_{2}\mathtt{D}_{2}\right)$

$$\left\{\left|\mathrm{DD}\right\rangle\!\left\langle\mathrm{DD}\right|, \left|\mathrm{DS}\right\rangle\!\left\langle\mathrm{DS}\right|, \left|\mathrm{DS}\right\rangle\!\left\langle\mathrm{SD}\right|, \left|\mathrm{SD}\right\rangle\!\left\langle\mathrm{SD}\right|, \left|\mathrm{DS}\right\rangle\!\left\langle\mathrm{AA}\right|, \left|\mathrm{AA}\right\rangle\!\left\langle\mathrm{SD}\right|, \left|\mathrm{SS}\right\rangle\!\left\langle\mathrm{SS}\right|\right\}$$

introduced previously in Eq. (21). These fragment coverings can be represented by the following transfer matrix

$${}_{2}\mathbb{D}_{2} = \begin{array}{c} \\ \left|\mathrm{SS}\right\rangle \\ \left|\mathrm{SD}\right\rangle \\ \left|\mathrm{AA}\right\rangle \\ \left|\mathrm{DS}\right\rangle \\ \left|\mathrm{DD}\right\rangle \end{array} \begin{array}{c} \\ \to \\ \to \\ \to \\ \to \\ \to \end{array} \begin{array}{c} \overline{\left\langle\mathrm{SS}\right|} \\ \downarrow \end{array} \begin{array}{c} \overline{\left\langle\mathrm{SD}\right|} \\ \downarrow \end{array} \begin{array}{c} \overline{\left\langle\mathrm{AA}\right|} \\ \downarrow \end{array} \begin{array}{c} \overline{\left\langle\mathrm{DS}\right|} \\ \downarrow \end{array} \begin{array}{c} \overline{\left\langle\mathrm{DD}\right|} \\ \downarrow \end{array} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{40}$$

The rows of the transfer matrix are indexed by unique labels consisting of covering characters for the left interface of the analyzed fragment, and the columns of the transfer matrix, by the corresponding labels for the right interface. The elements of the transfer matrix can assume only two values,

0 and 1, where 1 indicates that $\big|\mathrm{XY}\big\rangle\big\langle\mathrm{ZV}\big|$, formed by combining the left interface covering $\big|\mathrm{XY}\big\rangle \equiv \big|\,\mathrm{cov}\,(e_1)\;\;\mathrm{cov}\,(e_3)\big\rangle$ with the right interface covering $\big\langle\mathrm{ZV}\big| \equiv \big\langle\,\mathrm{cov}\,(e_2)\;\;\mathrm{cov}\,(e_4)\big|$, belongs to $\mathrm{covs}\,(_2\mathtt{D}_2)$, while 0 indicates that $\big|\mathrm{XY}\big\rangle\big\langle\mathrm{ZV}\big|$ corresponds to no valid covering of the fragment $_2\mathtt{D}_2$.

Similar transfer matrices can be introduced for any fragment F. For example, for $_1\mathtt{D}_1$ and $_1\mathtt{W}_2$ the corresponding transfer matrices $_1\mathbb{D}_1$ and $_1\mathbb{W}_2$ are given by

$$
{}_1\mathbb{W}_2 \;=\; \begin{array}{c} \\ |\mathrm{S}\rangle \to \\ |\mathrm{D}\rangle \to \end{array} \begin{array}{c} \begin{array}{ccccc} \langle\mathrm{SS}| & \langle\mathrm{SD}| & \langle\mathrm{AA}| & \langle\mathrm{DS}| & \langle\mathrm{DD}| \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \end{array} \\ \left[\begin{array}{ccccc:c} 0 & 1 & 1 & 1 & 0 \\ \hdashline 0 & 0 & 0 & 0 & 1 \end{array}\right] \end{array} \qquad {}_1\mathbb{D}_1 \;=\; \begin{array}{c} \\ |\mathrm{S}\rangle \to \\ |\mathrm{D}\rangle \to \end{array} \begin{array}{c} \begin{array}{cc} \langle\mathrm{S}| & \langle\mathrm{D}| \\ \downarrow & \downarrow \end{array} \\ \left[\begin{array}{c:c} 1 & 0 \\ \hdashline 0 & 1 \end{array}\right] \end{array} \tag{41}
$$

while for the fragment $_2\mathtt{W}_3$, the transfer matrix $_2\mathbb{W}_3$ is given by

$$
{}_2\mathbb{W}_3 \;=\; \begin{array}{c} \\ |\mathrm{SS}\rangle \to \\ |\mathrm{SD}\rangle \to \\ |\mathrm{AA}\rangle \to \\ |\mathrm{DS}\rangle \to \\ |\mathrm{DD}\rangle \to \end{array} \begin{array}{c} \begin{array}{cccccccccccc} \langle\mathrm{SSS}| & \langle\mathrm{SSD}| & \langle\mathrm{SAA}| & \langle\mathrm{SDS}| & \langle\mathrm{AAS}| & \langle\mathrm{DSS}| & \langle\mathrm{SDD}| & \langle\mathrm{AAD}| & \langle\mathrm{DSD}| & \langle\mathrm{DAA}| & \langle\mathrm{DDS}| & \langle\mathrm{DDD}| \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \end{array} \\ \left[\begin{array}{cccccc:cccccc} 0 & 1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hdashline 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 0 \\ \hdashline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right] \end{array} \tag{42}
$$

Note that there is no need to consider separately the matrices $_{k+1}\mathbb{N}_k$ and $_k\mathbb{U}_k$. Owing to the mirror symmetry $_k\mathtt{D}_k \leftrightarrow {}_k\mathtt{U}_k$ and $_k\mathtt{W}_{k+1} \leftrightarrow {}_{k+1}\mathtt{N}_k$ discussed above, we can write

$$
{}_k\mathbb{U}_k \;=\; {}_k\mathbb{D}_k^{\dagger} \tag{43}
$$

$$
{}_{k+1}\mathbb{N}_k \;=\; {}_k\mathbb{W}_{k+1}^{\dagger} \tag{44}
$$

where the conjugation $(\,)^{\dagger}$ corresponds to a standard matrix transposition. Note also that non-zero values can appear only in the diagonal blocks of

the transfer matrices ${}_k\mathbb{D}_k$ and ${}_k\mathbb{W}_{k+1}$

$$ {}_k\mathbb{D}_k = \begin{bmatrix} {}^0_k\mathbb{D}^0_k & \mathbb{O} & \dots & \mathbb{O} \\ \mathbb{O} & {}^1_k\mathbb{D}^1_k & \ddots & \vdots \\ \vdots & \ddots & \ddots & \mathbb{O} \\ \mathbb{O} & \dots & \mathbb{O} & {}^k_k\mathbb{D}^k_k \end{bmatrix} \tag{45} $$

$$ {}_k\mathbb{W}_{k+1} = \begin{bmatrix} \mathbb{O} & {}^0_k\mathbb{W}^1_{k+1} & \mathbb{O} & \dots & \mathbb{O} \\ \vdots & \ddots & {}^1_k\mathbb{W}^2_{k+1} & \ddots & \vdots \\ \vdots & & \ddots & \ddots & \mathbb{O} \\ \mathbb{O} & \dots & \dots & \mathbb{O} & {}^k_k\mathbb{W}^{k+1}_{k+1} \end{bmatrix} \tag{46} $$

which is a direct consequence of Theorem 1. The diagonal blocks ${}^j_k\mathbb{D}^j_k$ and ${}^j_k\mathbb{W}^{j+1}_{k+1}$ are indexed by the order $j = \mathrm{ord}\,(|\mathtt{F}\rangle)$ determined by the labels of the covering characters of the left interface $|\mathtt{F}\rangle$ for a given block of the analyzed fragment $\mathtt{F} = {}_k\mathtt{D}_k$ or $\mathtt{F} = {}_k\mathtt{W}_{k+1}$. A recursive algorithm for constructing ${}^j_k\mathbb{D}^j_k$ and ${}^j_k\mathbb{W}^{j+1}_{k+1}$ is discussed below.

4.6 Dimensions of transfer matrices

The dimensions of transfer matrices ${}_k\mathbb{D}_k$ and ${}_k\mathbb{W}_{k+1}$ are determined by the number of valid interface coverings. According to Theorem 3(a), a valid covering of an interface of length k is represented by a k-letter word (a label) formed from the double letter AA and/or the letters D and S, concatenated in any order.

Let us denote by I_k the set of all possible valid labels of length k. By inspection of Eqs. (40), (41), and (42), we have

$$ I_1 = \{\mathrm{S}, \mathrm{D}\} $$
$$ I_2 = \{\mathrm{SS}, \mathrm{SD}, \mathrm{AA}, \mathrm{DS}, \mathrm{DD}\} $$
$$ I_3 = \{\mathrm{SSS}, \mathrm{SSD}, \mathrm{SAA}, \mathrm{SDS}, \mathrm{AAS}, \mathrm{DSS}, \mathrm{SDD}, \mathrm{AAD}, \mathrm{DSD}, \mathrm{DAA}, \mathrm{DDS}, \mathrm{DDD}\} $$

Any set I_k with $k \geq 3$ can be generated recursively by concatenation

$$I_k = \big\{\mathrm{S\,t} \,|\, \mathrm{t} \in I_{k-1}\big\} \cup \big\{\mathrm{AA\,t} \,|\, \mathrm{t} \in I_{k-2}\big\} \cup \big\{\mathrm{D\,t} \,|\, \mathrm{t} \in I_{k-1}\big\} \tag{47}$$

The three subsets in Eq. (47) are disjoint, because the first letter in the labels is different for each subset. Consequently we obtain a recursive formula for the cardinality of I_k

$$|I_k| = 2|I_{k-1}| + |I_{k-2}| \tag{48}$$

with the initial conditions $|I_1| = 2$ and $|I_2| = 5$. It is convenient to extend this formula to $k = 0$, where we interpret I_0 as a set containing one empty label. Clearly, $|I_0| = 1$. The resulting sequence

$$\big(|I_k| : k \in \mathbb{N}_0\big) = (1, 2, 5, 12, 29, 70, 169, 408, 985, 2378, 5741, \ldots) \tag{49}$$

usually referred to as Pell numbers P_k, is identical (up to the offset) to the sequence A000129 in OEIS [70]. The generating function for $|I_k|$ is $\big(1 - 2t - t^2\big)^{-1}$ and an explicit expression for $|I_k|$ is given by [70]

$$|I_k| = P_{k+1} = \sum_{j=0}^{\lfloor \frac{k}{2} \rfloor} \tbinom{k+1}{2j+1}\, 2^j \tag{50}$$

The dimensions of transfer matrices are readily expressed via Pell numbers. We have

$$\begin{aligned} {}_k\mathbb{D}_k &\in M_{|I_k|\times|I_k|} & {}_{k+1}\mathbb{N}_k &\in M_{|I_{k+1}|\times|I_k|} \\ {}_k\mathbb{U}_k &\in M_{|I_k|\times|I_k|} & {}_k\mathbb{W}_{k+1} &\in M_{|I_k|\times|I_{k+1}|} \end{aligned} \tag{51}$$

4.6.1 Delannoy numbers

A valid label $\mathrm{t} \in I_k$ assigns definite covering characters to all edges of some interface i of length k. Hence, via Eqs. (12) and (15), we can attribute a definite order $\mathrm{ord}\,(\mathrm{t})$ to every label t. For a label of length k, the minimal order (generated by the label SS...SS) is 0, and the maximal order (generated by the label DD...DD) is k.

Let us denote by I_k^j the set of all valid labels of length k and order j. Clearly, the family $\left\{ I_k^j : j = 0, \ldots, k \right\}$ is a partition of I_k, so we have

$$|I_k| = \sum_{j=0}^{k} \left| I_k^j \right| \tag{52}$$

By inspection of Eqs. (40), (41), and (42), we have

$$I_1^0 = \{\mathrm{S}\} \qquad I_1^1 = \{\mathrm{D}\}$$

$$I_2^0 = \{\mathrm{SS}\} \qquad I_2^1 = \{\mathrm{SD}, \mathrm{AA}, \mathrm{DS}\} \qquad I_2^2 = \{\mathrm{DD}\}$$

$$I_3^0 = \{\mathrm{SSS}\} \qquad I_3^3 = \{\mathrm{DDD}\}$$

$$I_3^1 = \{\mathrm{SSD}, \mathrm{SAA}, \mathrm{SDS}, \mathrm{AAS}, \mathrm{DSS}\} \qquad I_3^2 = \{\mathrm{SDD}, \mathrm{AAD}, \mathrm{DSD}, \mathrm{DAA}, \mathrm{DDS}\}$$

Any set I_k^j with $k \geq 3$ and $0 \leq j \leq k$ can be generated recursively as

$$I_k^j = \left\{ \mathrm{S\,t} \,|\, \mathrm{t} \in I_{k-1}^j \right\} \cup \left\{ \mathrm{AA\,t} \,|\, \mathrm{t} \in I_{k-2}^{j-1} \right\} \cup \left\{ \mathrm{D\,t} \,|\, \mathrm{t} \in I_{k-1}^{j-1} \right\} \tag{53}$$

where the extraneous sets I_k^j with $j < 0$ or $j > k$ are considered to be empty. For convenience of the exposition, we define also the set I_0^0 containing one empty label of order 0. Again, in analogy with Eqs. (47) and (48), we obtain from Eq. (53) a recurrence relation for $\left| I_k^j \right|$ given by

$$\left| I_k^j \right| = \left| I_{k-1}^j \right| + \left| I_{k-2}^{j-1} \right| + \left| I_{k-1}^{j-1} \right| \tag{54}$$

with the initial conditions $\left| I_0^0 \right| = \left| I_1^0 \right| = \left| I_1^1 \right| = 1$ and $\left| I_k^j \right| = 0$ for $j < 0$ or $j > k$. The triangle generated by this recurrence, which begins as

$$\begin{array}{ccccccc} & & & 1 & & & \\ & & 1 & & 1 & & \\ & 1 & & 3 & & 1 & \\ 1 & & 5 & & 5 & & 1 \\ & 1 & & 7 & & 13 & & 7 & & 1 \\ 1 & & 9 & & 25 & & 25 & & 9 & & 1 \end{array} \tag{55}$$

can be identified as a triangle of Delannoy numbers $T(k, j) \equiv D(k-j, j)$ ap-

pearing as the sequence A008288 in OEIS [71]. Delannoy numbers $D(m,n)$ have various combinatorial interpretations, including, among others, the number of paths from $(0,0)$ in a rectangular grid to the point (m,n), using only single steps $(1,0),(0,1)$, and $(1,1)$. This particular interpretation is closely related to our problem. If we represent a label of length k and order j as a point $(k-j,j)$ in a rectangular grid, and the covering characters S, D, and AA as the steps $(1,0),(0,1)$, and $(1,1)$, respectively, then the number $\left|I_k^j\right|$ of different labels of length k and order j is equal to the number $D(k-j,j)$ of paths from $(0,0)$ (i.e., from an empty label) to the point $(k-j,j)$ using only the steps $(1,0),(0,1)$, and $(1,1)$.

The corresponding generating function obtained readily from Eq. (54)

$$\sum_{k=0}^{\infty}\sum_{j=0}^{k}\left|I_k^j\right| t^j z^k = \frac{1}{1-z-tz-tz^2} \tag{56}$$

can be expanded in z and t to produce closed-form formulas [71]

$$\begin{aligned}\left|I_k^j\right| &= T(k,j) = D(k-j,j) \\ &= \sum_{i=0}^{\min(k-j,j)}\binom{k-i}{j}\binom{j}{i} = \sum_{i=0}^{\min(k-j,j)}\binom{k-j}{i}\binom{j}{i}2^i\end{aligned} \tag{57}$$

The dimensions of the diagonal blocks ${}_k^j\mathbb{D}_k^j$ and ${}_k^j\mathbb{W}_{k+1}^{j+1}$ of the transfer matrices ${}_k\mathbb{D}_k$ and ${}_k\mathbb{W}_{k+1}$ are readily expressed via Dellanoy numbers. We have

$$\begin{aligned}{}_k^j\mathbb{D}_k^j &\in M_{\left|I_k^j\right|\times\left|I_k^j\right|} & {}_k^j\mathbb{W}_{k+1}^{j+1} &\in M_{\left|I_k^j\right|\times\left|I_{k+1}^{j+1}\right|} \\ {}_k^j\mathbb{U}_k^j &\in M_{\left|I_k^j\right|\times\left|I_k^j\right|} & {}_{k+1}^{j+1}\mathbb{N}_k^j &\in M_{\left|I_{k+1}^{j+1}\right|\times\left|I_k^j\right|}\end{aligned} \tag{58}$$

4.7 Lexicographic order for interface coverings

Consider the function $\pi : \{S,A,D\} \to \{0,1,2\}$ defined as follows

$$\pi(\mathrm{S}) = 0 \qquad \pi(\mathrm{A}) = 1 \qquad \pi(\mathrm{D}) = 2 \tag{59}$$

and its extensions $\pi_k : I_k \to \mathbb{N}$ defined for each k-letter label $I_k \ni \mathrm{t} = L_k \ldots L_3 L_2 L_1$ with $L_i \in \{S, D, A\}$ as follows

$$\pi_k(\mathrm{t}) = \pi(L_k) \ldots \pi(L_3)\, \pi(L_2)\, \pi(L_1)_{(3)} \tag{60}$$

$$= \sum_{i=1}^{k} \pi(L_i) \cdot 3^{i-1} \tag{61}$$

where Eq. (60) gives the representation of the integer $\pi_k(\mathrm{t})$ in base 3, and Eq. (61) gives the usual decimal representation. It is clear that if $\mathrm{t}_1, \mathrm{t}_2 \in I_k$ are different, then the integers $\pi_k(\mathrm{t}_1)$ and $\pi_k(\mathrm{t}_2)$ assigned to them are also different, since they differ in their base 3 representation in at least one digit. This property, along with the well-ordering of $\mathbb{N}$, allows us to introduce a lexicographic order $\prec$ on the set I_k of interface coverings

$$\forall\, \mathrm{t}_1, \mathrm{t}_2 \in I_k : \ \mathrm{t}_1 \prec \mathrm{t}_2 \iff \pi_k(\mathrm{t}_1) < \pi_k(\mathrm{t}_2) \tag{62}$$

For example, for the two labels SDAADDS and DSSAADS from I_7, we have SDAADDS $\prec$ DSSAADS because $\pi_7(\mathrm{SDAADDS}) = 0211220_{(3)} = 618 < \pi_7(\mathrm{DSSAADS}) = 2001120_{(3)} = 1500$.

The lexicographic order $\prec$ allows us to sort the labels in I_k in increasing order. The lexicographic order imposed in this way on I_1, I_2, and I_3 is

$$I_1 : \ \mathrm{S} \prec \mathrm{D} \tag{63}$$

$$I_2 : \ \mathrm{SS} \prec \mathrm{SD} \prec \mathrm{AA} \prec \mathrm{DS} \prec \mathrm{DD} \tag{64}$$

$$I_3 : \ \mathrm{SSS} \prec \mathrm{SSD} \prec \mathrm{SAA} \prec \mathrm{SDS} \prec \mathrm{SDD} \prec \mathrm{AAS} \prec \mathrm{AAD} \prec \mathrm{DSS} \prec \mathrm{DSD}, \tag{65}$$
$$\mathrm{DSD} \prec \mathrm{DAA} \prec \mathrm{DDS} \prec \mathrm{DDD}$$

Since $I_k^j \subset I_k$, the lexicographic order in I_k is naturally inherited by every I_k^j. In the following sections, we assume that labels in every I_k and I_k^j are always sorted in the lexicographic order.

In practice, it is easier to generate immediately the labels for each I_k and I_k^j in the lexicographic order rather than sort them. In fact, the recursive algorithm based on Eq. (47) generates each I_k for $k \geq 3$ in lexicographic order if I_1 and I_2 are taken in lexicographic order given by

Eqs. (63) and (64), respectively. Similarly, the recursive algorithm based on Eq. (53) generates each I_k^j for $k \geq 3$ and $0 \leq j \leq k$ in lexicographic order if $I_2^1 = \{\mathrm{SD} \prec \mathrm{AA} \prec \mathrm{DS}\}$ is taken in lexicographic order.

4.8 Recursive generation of transfer matrices

We have shown in Eqs. (43), (44), (45), and (46) that the only quantities needed to determine the transfer matrices ${}_k\mathbb{U}_k$, ${}_k\mathbb{D}_k$, ${}_{k+1}\mathbb{N}_k$, and ${}_k\mathbb{W}_{k+1}$ are the submatrices ${}_k^j\mathbb{D}_k^j$ and ${}_k^j\mathbb{W}_{k+1}^{j+1}$, whose dimensions have been given by Eq. (58). Every matrix ${}_k^j\mathbb{D}_k^j$ with $k \geq 3$ and $0 < j < k$ can be conveniently formed by arranging together smaller size matrices

$$
{}_k^j\mathbb{D}_k^j = \left[\begin{array}{c:c}
{}_{k-1}^{j}\mathbb{D}_{k-1}^{j} & \mathbb{O} \\
\hdashline
{}_{k-2}^{j-1}\mathbb{W}_{k-1}^{j} & \\
\hdashline
{}_{k-1}^{j-1}\mathbb{W}_{k}^{j} &
\end{array}\right] \tag{66}
$$

while every matrix ${}_k^j\mathbb{W}_{k+1}^{j+1}$ with $k \geq 3$ and $0 < j < k$ can be formed as

$$
{}_k^j\mathbb{W}_{k+1}^{j+1} = \left[\begin{array}{c:c}
{}_{k-1}^{j}\mathbb{W}_{k}^{j+1} & {}_{k-1}^{j}\mathbb{D}_{k-1}^{j} \\
\hdashline
\mathbb{O} & {}_k^j\mathbb{D}_k^j
\end{array}\right] \tag{67}
$$

These two formulas are simple consequences of the partial assignment step analogous to that shown in Eq. (31); details are explained in the next few paragraphs. Eqs. (66) and (67) are not applicable when $k = 1, 2$ and when

$j = 0$ or $j = k$; in these special cases we have

$$ {}^{0}_{k}\mathbb{D}^{0}_{k} \;=\; {}^{k}_{k}\mathbb{D}^{k}_{k} \;=\; {}^{k}_{k}\mathbb{W}^{k+1}_{k+1} \;=\; \left[\begin{array}{c} 1 \end{array}\right] \tag{68} $$

$$ {}^{0}_{k}\mathbb{W}^{1}_{k+1} \;=\; \left[\begin{array}{ccccc} 1 & 1 & 1 & \cdots & 1 \end{array}\right] \in M_{1\times(2k+1)} \tag{69} $$

$$ {}^{1}_{2}\mathbb{D}^{1}_{2} \;=\; \left[\begin{array}{ccc} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 1 & 1 \end{array}\right] \qquad {}^{1}_{2}\mathbb{W}^{2}_{3} \;=\; \left[\begin{array}{ccccc} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 \end{array}\right] \tag{70} $$

In a sense, Eqs. (66) and (67) can be considered as recurrence relations for ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$ with the boundary conditions given by Eqs. (68)–(70). These formulas allow one to generate the explicit form of ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$ for arbitrary values of k and j that may be needed in practical applications. Solutions of these recurrence relations, i.e., closed-form explicit formulas for arbitrary ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$, remain unknown at present.

The recursive algorithm given by Eqs. (66)–(70) for generating ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$ is based on the observation that all the labels in I^{j}_{k} and I^{j+1}_{k+1} with S in the first position precede those with A in the first position, and those in turn precede those with D in the first position. This feature allows to partition ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$ into nine blocks each

$$ \left[\begin{array}{c:c:c} \mathbb{M}_{\mathrm{SS}} & \mathbb{M}_{\mathrm{SA}} & \mathbb{M}_{\mathrm{SD}} \\ \hdashline \mathbb{M}_{\mathrm{AS}} & \mathbb{M}_{\mathrm{AA}} & \mathbb{M}_{\mathrm{AD}} \\ \hdashline \mathbb{M}_{\mathrm{DS}} & \mathbb{M}_{\mathrm{DA}} & \mathbb{M}_{\mathrm{DD}} \end{array}\right] \tag{71} $$

where the first subscript $\mathrm{X} \in \{\mathrm{S}, \mathrm{A}, \mathrm{D}\}$ denotes row labels starting with X, and the second subscript $\mathrm{Y} \in \{\mathrm{S}, \mathrm{A}, \mathrm{D}\}$ denotes column labels starting with Y. Dimensions and the structure of the block matrices $\mathbb{M}_{\mathrm{XY}}$ are shown in Fig. 8. The partition is a direct consequence of the recurrence relations (27)–(30). The structure of the block matrices $\mathbb{M}_{\mathrm{XY}}$ can be probably best understood on an example discussed in the next paragraphs.

Let us determine the explicit structure of the matrix ${}^{1}_{4}\mathbb{D}^{1}_{4}$. The analysis is based on the graphical proof of Eq. (30) given by Eq. (31) for the partial covering character assignment to the interface edges of the fragment ${}_{4}\mathtt{D}_{4}$.

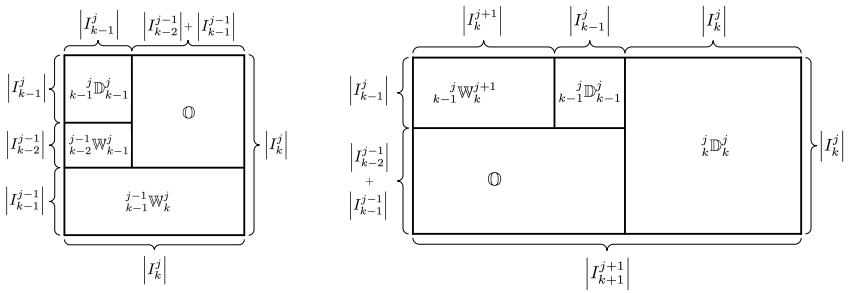


Figure 8. Graphical representation of the block structure of the matrices ${}^{j}_{k}\mathbb{D}^{j}_{k}$ (left panel) and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$ (right panel) allow us to design a recursive algorithm generating both set of matrices for arbitrary values of k and j.

From Eq. (58) we know that ${}^{1}_{4}\mathbb{D}^{1}_{4} \in M_{7\times 7}$ because according to Eq. (57) there exist 7 labels of length 4 and of order 1

$$\begin{aligned} I^1_4 &= \left\{ \mathrm{S\,t} \,|\, \mathrm{t} \in I^1_3 \right\} \cup \left\{ \mathrm{AA\,t} \,|\, \mathrm{t} \in I^0_2 \right\} \cup \left\{ \mathrm{D\,t} \,|\, \mathrm{t} \in I^0_3 \right\} \\ &= \{\mathrm{SSSD} \prec \mathrm{SSAA} \prec \mathrm{SSDS} \prec \mathrm{SAAS} \prec \mathrm{SDSS} \prec \mathrm{AASS} \prec \mathrm{DSSS}\} \end{aligned}$$

that can be generated in this form by Eq. (53). Since the ordered set I^1_4 is used to index both rows and columns of ${}^{1}_{4}\mathbb{D}^{1}_{4}$, we see that

$${}^{1}_{4}\mathbb{D}^{1}_{4} = \left[\begin{array}{c:c:c} \mathbb{M}_{\mathrm{SS}} \in M_{5\times 5} & \mathbb{M}_{\mathrm{SA}} \in M_{5\times 1} & \mathbb{M}_{\mathrm{SD}} \in M_{5\times 1} \\ \hdashline \mathbb{M}_{\mathrm{AS}} \in M_{1\times 5} & \mathbb{M}_{\mathrm{AA}} \in M_{1\times 1} & \mathbb{M}_{\mathrm{AD}} \in M_{1\times 1} \\ \hdashline \mathbb{M}_{\mathrm{DS}} \in M_{1\times 5} & \mathbb{M}_{\mathrm{DA}} \in M_{1\times 1} & \mathbb{M}_{\mathrm{DD}} \in M_{1\times 1} \end{array}\right] \tag{72}$$

because there are 5 labels starting with S, 1 label starting with A, and 1 label starting with D. The structure of the blocks $\mathbb{M}_{\mathrm{XY}}$ with X,Y $\in$ {S, A, D} follows directly from Eq. (31), which shows—among other facts—that if the first interface edge e_1 in ${}_4\mathtt{D}_4$ has the covering character S assigned to it, then the second interface edge e_2 in ${}_4\mathtt{D}_4$ also has S assigned to it. This immediately leads to a conclusion that all the coverings of the fragment ${}_4\mathtt{D}_4$ with $\mathrm{cov}\,(e_1) = \mathrm{S}$ and $\mathrm{cov}\,(e_2) \in$ {D,A} are not valid. Consequently, all entries of the transfer matrix ${}^{1}_{4}\mathbb{D}^{1}_{4}$ indexed by row labels starting with

S and by column labels starting with D or A are 0. This, in turn, leads to the observation that both $\mathbb{M}_{\mathrm{SA}}$ and $\mathbb{M}_{\mathrm{SD}}$ are null matrices, $\mathbb{M}_{\mathrm{SA}} = \mathbb{M}_{\mathrm{SD}} = \mathbb{O}_{5\times 1}$. The validity of the coverings of the fragment ${}_4\mathtt{D}_4$ with $\mathrm{cov}\,(e_1) = \mathrm{S}$ and $\mathrm{cov}\,(e_2) = \mathrm{S}$ depends whether the covering characters for the remaining interface edges $e_3, \ldots, e_k$ form a valid covering for the smaller subfragment ${}_3\mathtt{D}_3$, which, in turn, can be expressed as the transfer matrix ${}_3^1\mathbb{D}_3^1$, owing to the fact that the partial assignment $\mathrm{cov}\,(e_1) = \mathrm{S}$ and $\mathrm{cov}\,(e_2) = \mathrm{S}$ does not contribute to the order of neither left nor right interface of ${}_4\mathtt{D}_4$. We have then $\mathbb{M}_{\mathrm{SS}} = {}_3^1\mathbb{D}_3^1$.

Similar reasoning based on Eq. (31) for $\mathrm{cov}\,(e_1) = \mathrm{A}$ shows that $\mathbb{M}_{\mathrm{AA}} = \mathbb{M}_{\mathrm{AD}} = \mathbb{O}_{1\times 1}$, because $\mathrm{cov}\,(e_1) = \mathrm{A}$ and $\mathrm{cov}\,(e_2) \in \{\mathrm{D,A}\}$ cannot represent a valid covering of the fragment ${}_4\mathtt{D}_4$. On the other hand, $\mathbb{M}_{\mathrm{AS}} = {}_2^0\mathbb{W}_3^1$, because valid coverings of the fragment ${}_4\mathtt{D}_4$ with $\mathrm{cov}\,(e_1) = \mathrm{A}$ necessarily induce also $\mathrm{cov}\,(e_2) = \mathrm{S}$ and $\mathrm{cov}\,(e_3) = \mathrm{A}$, while the covering characters for the remaining interface edges $e_4, \ldots, e_k$ need to form a valid covering of the subfragment ${}_2\mathtt{W}_3$. Since $\mathrm{cov}\,(e_1) = \mathrm{cov}\,(e_3) = \mathrm{A}$ contributes 1 to the order of the left interface of ${}_4\mathtt{D}_4$, and $\mathrm{cov}\,(e_2) = \mathrm{S}$ contributes 0 to the order of the right interface of ${}_4\mathtt{D}_4$, we are interested in valid coverings of the fragment ${}_2\mathtt{W}_3$ with the left interface order of $1 - 1 = 0$ and the right interface order of $1 - 0 = 1$, which can be expressed as the transfer matrix ${}_2^0\mathbb{W}_3^1$.

The situation is simpler for $\mathrm{cov}\,(e_1) = \mathrm{D}$. Eq. (31) shows that selecting the covering character D for e_1 contributes 1 to the order of the left interface of ${}_4\mathtt{D}_4$, but it does not influence the choice of covering characters for other interface edges in ${}_4\mathtt{D}_4$. Consequently, valid coverings of ${}_4\mathtt{D}_4$ with $\mathrm{cov}\,(e_1) = \mathrm{D}$ are obtained by choosing valid coverings of the subfragment ${}_3\mathtt{W}_4$ with the left interface order of $1 - 1 = 0$ and the right interface order of $1 - 0 = 1$, a process which can be controlled using the transfer matrix ${}_3^0\mathbb{W}_4^1$. We have then

$$\left[\begin{array}{c:c:c} \mathbb{M}_{\mathrm{DS}} & \mathbb{M}_{\mathrm{DA}} & \mathbb{M}_{\mathrm{DD}} \end{array}\right] = {}_3^0\mathbb{W}_4^1$$

and the matrix ${}_4^1\mathbb{D}_4^1$ can be conveniently formed by arranging together

smaller size matrices ${}^{1}_{3}\mathbb{D}^{1}_{3}$, ${}^{0}_{2}\mathbb{W}^{1}_{3}$, ${}^{0}_{3}\mathbb{W}^{1}_{4}$, and $\mathbb{O} = \mathbb{O}_{6\times 2}$

$$ {}^{1}_{4}\mathbb{D}^{1}_{4} = \left[\begin{array}{c:c} {}^{1}_{3}\mathbb{D}^{1}_{3} & \mathbb{O} \\ \hdashline {}^{0}_{2}\mathbb{W}^{1}_{3} & \\ \hdashline \multicolumn{2}{c}{{}^{0}_{3}\mathbb{W}^{1}_{4}} \end{array}\right] = \left[\begin{array}{ccccc:cc} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 0 & 0 \\ \hdashline 1 & 1 & 1 & 1 & 1 & 0 & 0 \\ \hdashline 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{array}\right] \tag{73} $$

Similar reasoning for the fragment ${}_{3}\mathtt{W}_{4}$, based on Eq. (28) and a partial assignment step analogous to that shown in Eq. (31), shows that the transfer matrix ${}^{2}_{3}\mathbb{W}^{3}_{4}$ of size 5×7 can be conveniently formed by arranging together smaller size matrices ${}^{2}_{2}\mathbb{W}^{3}_{3}$, ${}^{2}_{2}\mathbb{D}^{2}_{2}$, ${}^{2}_{3}\mathbb{D}^{2}_{3}$, and $\mathbb{O} = \mathbb{O}_{4\times 2}$

$$ {}^{2}_{3}\mathbb{W}^{3}_{4} = \left[\begin{array}{cc:c} {}^{2}_{2}\mathbb{W}^{3}_{3} & {}^{2}_{2}\mathbb{D}^{2}_{2} & \\ \hdashline \multicolumn{2}{c:}{\mathbb{O}} & {}^{2}_{3}\mathbb{D}^{2}_{3} \end{array}\right] = \left[\begin{array}{cc:ccccc} 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ \hdashline 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 \end{array}\right] \tag{74} $$

The construction process explained here for the transfer matrices ${}^{1}_{4}\mathbb{D}^{1}_{4}$ and ${}^{2}_{3}\mathbb{W}^{3}_{4}$ can be applied to arbitrary size k and arbitrary order j transfer matrices ${}^{j}_{k}\mathbb{D}^{j}_{k}$ and ${}^{j}_{k}\mathbb{W}^{j+1}_{k+1}$, using the same block submatrix structure as derived here and generalized to an arbitrary value of k and j in Fig. 8 and in Eqs. (68), (69), and (70).

4.9 Enumeration of Clar covers

Eq. (11) shows that every armchair nanotube $(n,n)_d$ can be represented as a cyclic sequence of $2n$ fragments. Consequently, every Clar cover of $(n,n)_d$ can be specified as a sequence of $2n$ fragment coverings, in such a way that the right interface covering of the previous fragment is equal to the left interface covering of the next fragment in agreement with Lemma 4. Algebraically, enumeration of such coverings corresponds to the product of

a train of transfer matrices. The last matrix contraction—performed over the column index of the last matrix in the train and the row index of the first matrix in the train—corresponds to closing the planar patch into a tubular nanotube along the scission line, and can be formally represented as the trace of the entire matrix train product. Consequently, for integer values of d, the number $\mathcal{C}_{n,d}$ of Clar covers of $(n,n)_d$ is given by the following expressions

$$\begin{aligned} \mathcal{C}_{n,d} &= \mathrm{Tr}\left[\left({}_{d}\mathbb{D}_{d}\ {}_{d}\mathbb{U}_{d}\right)^{n}\right] = \mathrm{Tr}\left[\left({}_{d}\mathbb{U}_{d}\ {}_{d}\mathbb{D}_{d}\right)^{n}\right] \\ &= \sum_{j=0}^{d} \mathrm{Tr}\left[\left({}^{j}_{d}\mathbb{D}^{j}_{d}\ {}^{j}_{d}\mathbb{U}^{j}_{d}\right)^{n}\right] = \sum_{j=0}^{d} \mathrm{Tr}\left[\left({}^{j}_{d}\mathbb{U}^{j}_{d}\ {}^{j}_{d}\mathbb{D}^{j}_{d}\right)^{n}\right] \end{aligned} \tag{75}$$

while for half-integer values of d, the corresponding expressions are

$$\begin{aligned} \mathcal{C}_{n,d} &= \mathrm{Tr}\left[\left({}_{\lceil d\rceil}\mathbb{N}_{\lfloor d\rfloor}\ {}_{\lfloor d\rfloor}\mathbb{W}_{\lceil d\rceil}\right)^{n}\right] = \mathrm{Tr}\left[\left({}_{\lfloor d\rfloor}\mathbb{W}_{\lceil d\rceil}\ {}_{\lceil d\rceil}\mathbb{N}_{\lfloor d\rfloor}\right)^{n}\right] \\ &= \sum_{j=0}^{\lfloor d\rfloor} \mathrm{Tr}\left[\left({}^{j+1}_{\lceil d\rceil}\mathbb{N}^{j}_{\lfloor d\rfloor}\ {}^{j}_{\lfloor d\rfloor}\mathbb{W}^{j+1}_{\lceil d\rceil}\right)^{n}\right] = \sum_{j=0}^{\lfloor d\rfloor} \mathrm{Tr}\left[\left({}^{j}_{\lfloor d\rfloor}\mathbb{W}^{j+1}_{\lceil d\rceil}\ {}^{j+1}_{\lceil d\rceil}\mathbb{N}^{j}_{\lfloor d\rfloor}\right)^{n}\right] \end{aligned} \tag{76}$$

4.10 Zhang-Zhang polynomial

Eqs. (75) and (76) enumerate Clar covers of $(n,n)_d$, but they are not able to discriminate between Clar covers with different order (i.e., Clar covers containing a different number of aromatic sextets C_6). Fortunately, a slight modification of Eqs. (75) and (76) can resolve this shortcoming.

Let us first consider the function $\sigma : \{S, A, D\} \to \{0, 1/2\}$ defined as follows

$$\sigma\,(\mathrm{S}) = 0 \qquad \sigma\,(\mathrm{A}) = 1/2 \qquad \sigma\,(\mathrm{D}) = 0 \tag{77}$$

and its extensions $\sigma_k : I_k \to \mathbb{N}$ defined for each k-letter label $I_k \ni \mathrm{t} = L_k \ldots L_3 L_2 L_1$ with $L_i \in \{S, D, A\}$ as follows

$$\sigma_k(\mathrm{t}) = \sum_{i=1}^{k} \sigma\,(L_i) \tag{78}$$

Plainly speaking, the integer $\sigma_k(\mathrm{t})$ denotes the number of pairs AA in $\mathrm{t} \in I_k$ and could possibly be referred to as the Clar number of the interface covering determined by the label t.

Let $\mathbb{X}_d^j$ denote a square matrix with dimensions $|I_d^j| \times |I_d^j|$. Let the rows and columns of $\mathbb{X}_d^j$ be indexed by the labels $\mathrm{t}_m \in I_d^j$ sorted in lexicographic order, $\mathrm{t}_1 \prec \mathrm{t}_2 \prec \ldots \prec \mathrm{t}_{|I_d^j|}$. The entries of $\mathbb{X}_d^j$ are defined as follows

$$\left[\mathbb{X}_d^j\right]_{ml} = \begin{cases} x^{\sigma_d(\mathrm{t}_m)} & \text{for } m = l \\ 0 & \text{for } m \neq l \end{cases} \tag{79}$$

With the initial conditions given by the following expressions

$$\mathbb{X}_d^0 \;=\; \mathbb{X}_d^d \;=\; \begin{bmatrix} 1 \end{bmatrix} \qquad\qquad \mathbb{X}_2^1 \;=\; \begin{bmatrix} 1 & 0 & 0 \\ 0 & x & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{80}$$

the matrices $\mathbb{X}_d^j$ can be constructed in a recursive fashion induced by Eq. (53) as follows

$$\mathbb{X}_d^j = \left[\begin{array}{c:c:c} \mathbb{X}_{d-1}^j & \mathbb{O} & \mathbb{O} \\ \hdashline \mathbb{O} & x \cdot \mathbb{X}_{d-2}^{j-1} & \mathbb{O} \\ \hdashline \mathbb{O} & \mathbb{O} & \mathbb{X}_{d-1}^{j-1} \end{array}\right] \tag{81}$$

Now we are sufficiently equipped to define the ZZ polynomial of $(n,n)_d$, which is given by equations analogous to the previously derived Eqs. (75) and (76). We have

$$\begin{aligned} ZZ\left((n,n)_d, x\right) &= \sum_{j=0}^{d} \mathrm{Tr}\left[\left(\mathbb{X}_d^j \; {}_d^j\mathbb{D}_d^j \; \mathbb{X}_d^j \; {}_d^j\mathbb{U}_d^j\right)^n\right] \\ &= \sum_{j=0}^{d} \mathrm{Tr}\left[\left(\mathbb{X}_d^j \; {}_d^j\mathbb{U}_d^j \; \mathbb{X}_d^j \; {}_d^j\mathbb{D}_d^j\right)^n\right] \end{aligned} \tag{82}$$

while for half-integer values of d, the corresponding expressions are

$$ZZ\left((n,n)_d,x\right) = \sum_{j=0}^{\lfloor d \rfloor} \mathrm{Tr}\left[\left(\mathbb{X}^{j+1}_{\lceil d \rceil} \; {}^{j+1}_{\lceil d \rceil}\mathbb{N}^{j}_{\lfloor d \rfloor} \; \mathbb{X}^{j}_{\lfloor d \rfloor} \; {}^{j}_{\lfloor d \rfloor}\mathbb{W}^{j+1}_{\lceil d \rceil} \right)^n\right] \quad (83)$$

$$= \sum_{j=0}^{\lfloor d \rfloor} \mathrm{Tr}\left[\left(\mathbb{X}^{j}_{\lfloor d \rfloor} \; {}^{j}_{\lfloor d \rfloor}\mathbb{W}^{j+1}_{\lceil d \rceil} \; \mathbb{X}^{j+1}_{\lceil d \rceil} \; {}^{j+1}_{\lceil d \rceil}\mathbb{N}^{j}_{\lfloor d \rfloor} \right)^n\right]$$

5 Conclusions

The current study reports closed form formulas allowing one to determine the Zhang-Zhang polynomials—and consequently: the most important topological invariants—of zigzag nanotubes $(n,0)_d$ and armchair nanotubes $(n,n)_d$ with arbitrary diameter n and arbitrary length d. The ZZ polynomial of $(n,0)_d$, given by Eq. (10), is equal to 2^d. The derived formula shows that zigzag nanotubes permit only Kekulé structures and that their Clar number $Cl = 0$ in agreement with the previous result of Zhang and Wang [91]. Another interesting observation is that the number of Kekulé structures for zigzag nanotubes, $\mathcal{K} = 2^d$, does not depend on the diameter of the nanotube n but only on its length d.

To derive the ZZ polynomial formula for armchair nanotubes $(n,n)_d$, we have resorted to the recently developed interface theory of benzenoids [42], tailored here to the current problem. Five types of transfer matrices have been derived, constituting sufficient tools for computing ZZ polynomials for arbitrary armchair nanotubes $(n,n)_d$ using Eqs. (82) and (83). The developed transfer matrix technique seems to constitute a promising methodology for computing ZZ polynomials of various classes of aromatic hydrocarbons.

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