An Algorithm to Enumerate a Special Class of Digraphs: Application to Water Clusters*

Damir Vukičevića,** and Ante Graovacb,c

aFaculty of Science, Department of Mathematics, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia
bFaculty of Science, Department of Chemistry, University of Split, Nikole Tesle 12, HR-21000 Split, Croatia
cThe Ruđer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia

RECENTLY MIYAKE AND AIDA HAVE DEVELOPED A DIRECTED GRAPH MODEL AND RELATED ALGORITHM WHICH GENERATES ALL POSSIBLE TOPOLOGICALLY DISTINCT HYDROGEN-BONDED CLUSTERS OF WATER MOLECULES. HERE WE PRESENT A NEW ALGORITHM BASED ON RECURSIVE FUNCTIONS. NUMERICAL RESULTS SHOW THAT OUR ALGORITHM IS MUCH FASTER THAN THAT OF MIYAKE AND AIDA.

Keywords
digraphs
recursive algorithms
enumeration
optimization of algorithms
water clusters
hydrogen bonding

INTRODUCTION

The study of water clusters is continuously in the focus of scientific attention. Computational tasks to analyze stability and dynamics of such clusters are demanding.1-4 However, prior to any computation one has to enumerate all possible topologically distinct clusters. Here, the discrete mathematics plays an important role. One possible discrete model is to represent water clusters by a special class of directed graphs, i.e., digraphs, where vertices correspond to water molecules and arcs (directed bonds) to hydrogen bonds from proton-donor of one molecule to proton-acceptor of another water molecule. The procedure, which we further call the MA algorithm, to obtain all possible topologically distinct clusters has been developed by Miyake and Aida1,2 which have been able to enumerate all possible clusters with up to eight water molecules. As the number of topologically distinct clusters grows enormously with the number of water molecules in the cluster, it is of interest to develop an efficient graph algorithm6 to enumerate distinct clusters. Here, we present an algorithm which is much faster than the MA one as it is based on the recursive enumeration.

The underlying connected graph G representing a cluster of n water molecules is a graph on n vertices with some number, m, of edges, where an edge describes a presence of hydrogen bond between two water molecules. If, for each edge, we know which of its terminal vertices (water molecules) donates a proton and which one accepts this proton, then instead of G, we describe the totality of directed bonding by a digraph H. As a wa-
For a digraph $H$ the element $C_{ij}$ are marked as bolded. The corresponding elements in Figure 1a. Its non-zero elements above the main diagonal are marked as dotted. Here, we introduce the notion of canonical labeling. Let consider the adjacency matrix of graph shown in Figure 1a together with its adjacency matrix. A digraph shown together with its adjacency matrix in Figure 1c is equivalent to one shown in Figure 1b.

For e.g. clusters of three water molecules there are only two distinct undirected graphs: 3-cycle and a path of length 3. The underlying graph of the path cluster is shown in Figure 1a together with its adjacency matrix. There are three topologically distinct digraphs of path and one of them is shown with its adjacency matrix in Figure 1b. A digraph shown together with its adjacency matrix in Figure 1c is equivalent to one shown in Figure 1b.

![Figure 1. Underlying graph and two equivalent digraphs of path cluster of three water molecules with their adjacency matrices.](image)

**METHOD**

The MA method considers all possible adjacency matrices of underlying graphs. It proceeds further by eliminating graphs having vertices of degrees larger than 4, while this restriction is implemented as a core of our algorithm. However, both methods have to eliminate disconnected graphs and duplicates.

After having at disposal the underlying graphs, for each of them one has to consider all its corresponding digraphs satisfying the above restrictions on valencies. The MA method considers all possible orientations of edges and then eliminates those that don’t satisfy restrictions on valencies, where we adhere to the same restrictions, but we put them in the very core of our recursive algorithm.

The last step in both methods is to eliminate duplicates. Here, we introduce the notion of canonical labeling. Let consider the adjacency matrix of graph shown in Figure 1a. Its non-zero elements above the main diagonal are marked as bolded. The corresponding elements in adjacency matrices of two isomorphic digraphs shown in Figures 1b and 1c read as binary numbers are 11 and 00, respectively. The digraph with smaller, in general with the smallest among such numbers, we call canonically labeled digraph. Our method eliminates duplicates much quicker than the MA method, because we consider only the automorphisms of the underlying graph instead of considering all the permutations of vertices. Namely, as for a graph on $n$ vertices there are $n!$ permutations to be considered in the MA method, in our method one considers only a few automorphisms.

**ALGORITHM**

We use the following variables in our algorithm (and we assume that at the beginning of the execution of the program all variables are set to zero):

- **NumVertices** is the number of vertices of the graphs under consideration. It is the input given to the program (it is assumed that $NumVertices \geq 7$ as the results of enumeration for the graphs with lower number of vertices have been already given by Miyake and Aida1,2);
- **MaxDeg** is the maximum degree of the graph considered. Three options are successively examined: $MaxDeg = 2, 3, 4$;
- **$a$** is the matrix in which the adjacency matrix of a graph (respectively digraph) $G$ (respectively $H$) will be stored;
- **$deg$** (indeg, outdeg) are arrays in which degrees (indegrees, outdegrees) of each vertex are stored;
- **NumOfGraphs** stores the number of the graphs (digraphs) with the required properties;
- **NumOfAutomorphisms** stores the number of automorphisms of the observed graph;
- **Aut** stores all the automorphisms of the observed graph;
- **NumAut** is the number of the automorphisms of the observed graph;
- **NumEdges** stores the number of edges;
- **Edges** is $NumEdges \times 2$ array in which edges are stores. $Edges[i][1]$ and $Edges[i][2]$ are vertices that are incident to the $i$-th edge (the first and the second vertex uniquely determine the edge).

The algorithm (in the pseudo-code) is given below:

```plaintext
main()
For MaxDeg = 2,...,4
deg[1] = MaxDeg
For i = 2,..., MaxDeg + 1
da[1][i] = 1, da[i][1] = 1
deg[i] = 1
For i = MaxDeg + 2,...,NumVertices
da[1][i] = 0, da[i][1] = 0
deg[i] = 0
```

**RESULTS AND DISCUSSIONS**

This work was motivated by Miyake and Aids study of water clusters. The largest clusters they have been able to treat are those on 8 vertices. The algorithm presented...
here is able to go a step forward and up to now we have been able to enumerate topologically distinct clusters up to 12 vertices. Our algorithm is superior due to two facts:

1) it incorporates restrictive conditions on generation of unoriented graph into recursive function which results in much less number of generated objects,

2) it eliminates duplicates of digraphs using only automorphisms of the underlying graph instead of considering all permutations of vertices (hence, we consider only a few automorphisms of the graph instead of \( n! \) permutations to be considered in the method of Miyake and Aida).

As an example of the advantages of our algorithm, Ref. 10 gives an example in which it is shown that our algorithm needs to consider only 15 697 041 matrices as compared to 68 719 476 736 matrices to be considered in the method of Miyake and Aida.

The results obtained by the algorithm described here are summarized in table given below:

<table>
<thead>
<tr>
<th>Vertex(a)</th>
<th>Graph(b)</th>
<th>Digraph(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
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</tr>
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<td>12207</td>
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<td>89402</td>
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<td>460 066 726</td>
</tr>
<tr>
<td>12</td>
<td>6800637</td>
<td>7 644 586 673</td>
</tr>
</tbody>
</table>

(a) The number of the vertices.
(b) The number of the graphs generated.
(c) The number of the digraphs generated.

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REFERENCES


SAŽETAK

Algoritam za prebrojavanje posebne klase usmjerenih grafova: primijena na klastere molekula vode

Damir Vukičević i Ante Graovac

Miyake i Aida su nedavno predložile model zasnovan na usmjerenim grafovima i razvile algoritam za prebrojavanje svih mogućih, topološki različitih, vodikovim vezama povezanih, grozdova molekula vode. Ovdje je prikazan novi algoritam temeljen na rekurzivnim funkcijama. Brojčani rezultati pokazuju da je ovaj znatno brži od Miyake-Aida algoritma.