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Topological indices for nanoclusters

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ABSTRACT

Nanoclusters create the possibility of designing novel properties and devices based on finite structures, with small dimensions. Clusters are of interest for catalytic, optical, biochemical, and structural characteristics. We examine clusters of icosahedral, cuboctahedral, and decahedral symmetry. Examples of these types of structures are shown from gold and platinum nanoclusters. Starting with only the atomic coordinates, we create an adjacency and distance matrix that facilitates the calculation of topological indices, including the Wiener, hyper-Wiener, reverse Wiener, Szeged, Balaban, and Kirchhoff indices. Some of these indices correlate to properties of the cluster. We find these indices exhibit polynomial and inverse behavior as a function of an increasing number of shells. Additionally, all the indices can be modeled with power law curves, as a function of *N*, the number of atoms. The magnitude of the exponent in the power law is associated with an index. The asymptotic limits of the topological indices are determined as a function of *N*. A conjecture previously published on the asymptotic behavior of the Wiener index is experimentally confirmed.

1. Introduction

The phrase 'nanocluster' is often used to describe nanosized particles, since they can form structures, which strictly speaking are not crystalline in that they do not have bulk symmetry, whereas a cluster sized form with dimensions of 1–100 nm, may exist in the nano regime. There are many forms of shape and symmetry which may exist in nanosized materials [1], among them icosahedral, cuboctahedral, and decahedral.

Nanoclusters are created from atoms completing layers or shells sequentially giving rise to what has been phrased as 'magic numbers', or the number of atoms to complete a shell over a beginning layer. Thus, for some clusters, there has developed a large description of formulas, giving the relation of number of atoms, surface atoms, and bonds as a function of *L*, the number of shells in the cluster [2]. A summary of these formulas for icosahedral, cuboctahedral and decahedral clusters, for our purposes is given in Table 1. Note that the cuboctahedral clusters can be described as an FCC structure, whereas the icosahedral and decahedral are unique. Also, the cuboctahedral clusters require even and odd modeling, which is evident from the formulas, and applies to the modeling we do later. We examine the topological indices of nanoclusters with these symmetries for sizes up to several tens of thousands of atoms.

A large collection of results from metal nanoclusters exists, as metals comprise 75% of elements in the Periodic Table. These results are fairly recent with the majority occurring since the beginning of this century 15 years ago from developments in chemical synthesis [3,4]. In Fig. 1, we show reprints of gold and platinum nanoclusters having the icosahedral [5], cuboctahedral [6], and decahedral symmetry [7]. Gold and platinum clusters are especially of interest for catalytic purposes, as nano gold in particular has properties unknown in the bulk.

Topological indices can be traced back to the Wiener index in 1947 [8], although it was some time later in 1971 [9] that its status in the field of mathematical chemistry became established. Today there are many topological indices, and there have been fluctuations in the number of publications on these topics, with some indices becoming more relevant in the lexicon of topological chemistry. Recently, a C++ program detailing the numerical calculation of many of these indices has been made available [10] and we have rewritten these programs with a MATLAB program that calculates the adjacency and distance matrices from only the atomic coordinates. It is worthwhile to note that the C++ program only works for fullerenes, while our program only requires a coordinate file, and in principle any structure may be calculated. To be specific, any organic or inorganic structure where a coordinate file exists and where the nearest neighbors are well defined may be calculated. The adjacency matrix is calculated from a subset of the list of neighbors, since that is how we may define it. In a different type

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of analysis, we have modeled both fullerenes and nanoclusters [11]. In 2D, we have also looked at Penrose tilings [12].

The only previous results on clusters we are aware of are some calculations on nanoclusters of ZnS [13], which calculated the Wiener, hyper-Wiener and Szeged index. They also gave some correlations to properties of ZnS based on the topological indices. Although the property and design characteristics of molecular topology have been studied [14], our objective is to examine the computational modeling aspects of topological indices and nanoclusters.

2. Methods

As mentioned, we use a theoretical graph – network approach, with atoms at the vertices, and links as nearest neighbor bonds. An adjacency matrix is created which contains a 1 at position (i, j) if atom j is in the set of nearest neighbors of atoms i, i.e., when the distance r_{ij} is approximately equal to $r_{\min} = \min_{i \neq j} r_{ij}$. To allow for small deviations from the average bond length, we define i and j as nearest neighbors, and separate them from the rest by requiring that $r_{ij} < r_c$ where r_c is a threshold value, appropriate for the nanocluster. Thus,

$$\mathbf{A}(i,j) = \begin{cases} 1 \text{ if } r_{ij} < r_c \quad \text{and} \quad i \neq j \\ 0 \quad \text{otherwise} \end{cases} \tag{1}$$

As an alternative, we may consider the actual Euclidean distances in the adjacency matrix, i.e., replace every nonzero entry $\mathbf{A}(i, j)$ in the previous definition by the actual distance r_{ij} and keep the zeros.

Some topological indices are most easily calculated from the distance matrix, which is defined as

$$D_{ij} = \begin{cases} 0 & i = j \\ d_{ij} & i \neq j \end{cases} \tag{2}$$

Table 1
Magic number formulas for the icosahedral, cuboctahedral, and decahedral structures.

Definition	Notation	Cluster structure		
		ICO	CO (FCC)	DECA
Total number of atoms	N	$10\frac{L^3}{3} + 5L^2 + 11\frac{L}{3} + 1$	$10\frac{L^3}{3} + 5L^2 + 11\frac{L}{3} + 1$ (L even) $10\frac{L^3}{3} + 3L^2 - \frac{L}{3}$ (L odd)	$5\frac{L^3}{6} + \frac{L}{6}$
Number of surface atoms	N_S	$10L^2 + 2$	$10L^2 + 2$ (L even) $10L^2 - 4L$ (L odd)	$5L^2 - 10L + 7$
Number of bonds	N_B	$20L^3 + 12L^2 + 4L$	$20L^3 + 15L^2 + 7L$ (L even) $20L^3 - 8L$ (L odd)	$5L^3 - 15\frac{L^2}{2} + 7\frac{L}{2} - 1$

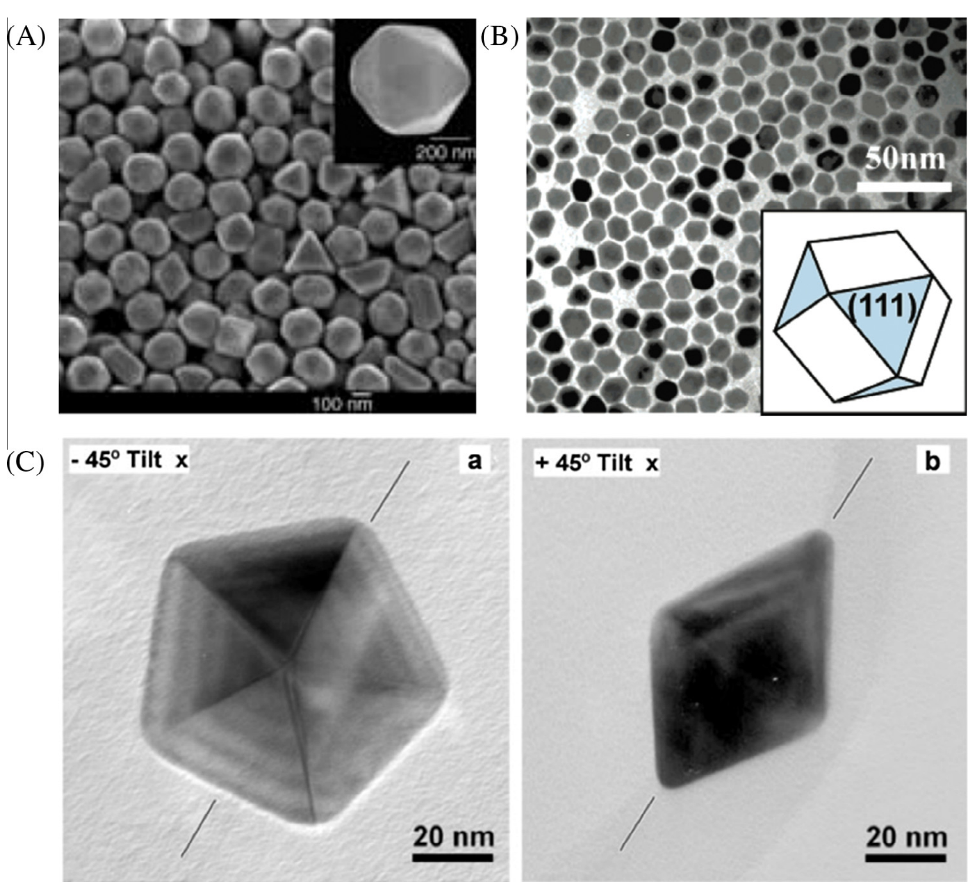

Fig. 1. Nanostructures examined in this manuscript. (A) Gold icosahedron [5]. (B) Platinum cuboctahedron [6]. (C) Gold decahedron [7]. Reprinted with permission.