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
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Geometrical Characteristics of Regular Polyhedra: Application to EXAFS Studies of Nanoclusters

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Abstract. EXAFS data modeling of nanoparticles can be done at a very high level of detail if regular polyhedral geometries are considered as possible structural models. Such geometries can be characterized by unique sequence of indices (coordination numbers) of the first few coordination shells that serve as a signature of a shape, size, morphology and packing model of atoms in the cluster. We wrote a suite of programs for cluster geometry generation and its pair radial distribution function analysis. The programs generate x,y,z coordinates and calculate the coordination numbers of the corresponding clusters for any order of a large number of regular polyhedra. We present the results for the first few nearest neighboring shells in the icosahedral, cuboctahedral, hcp structures for the small, 10-1000 atom clusters.

Keywords: Coordination numbers, magic numbers, nanoclusters.

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INTRODUCTION

EXAFS measurements of coordination numbers in nanoclusters contain their size- and shape-specific information that in some cases can be extracted from the data by modeling. For bare Au nanoclusters, a large number of different minimum-energy configurations have been proposed as structural motifs, of which closed shell icosahedral, truncated octahedral, cuboctahedral morphologies are among the most popular [1]. For supported clusters, a hemispherical shape is an alternative to theoretically possible monolayer and bilayer structures. Combination of high resolution transmission microscopy (HRTEM) and Z-contrast technique of scanning transmission electron microscopy provides robust structure, size and shape information of monodispersed nanoparticles. However, spatial (point to point) resolution of most electron microscopes is greater than 1 Å, i.e., far worse than that of EXAFS (0.04 Å). Moreover, EXAFS is a unique tool for studies of *in situ* transformations of nanoparticles, e.g., their nucleation and growth, or during catalysis. If the nanoparticles have narrow size distribution, EXAFS measurement can be interpreted in terms of the structure of individual nanoparticle (as opposed to the ensemble average, as in the case of polydispersed particles).

Evidence from HRTEM measurements in many supported and self-standing clusters indicates that they

adopt regular polyhedral shapes corresponding to “closed shell” systems of atoms. The number of atoms, N , in the closed shell clusters follows the sequence of magic numbers, unique for each cluster structure and morphology. Using an analogy with the adjacency matrix from graph theory, where each atom is a node and is connected by an edge to each of its first nearest neighbors, each cluster type can be specified by a unique set of indices: coordination numbers n_1, n_2, n_3 , etc. of the first, second, third etc. nearest neighbors. Such information, along with the multiple-scattering path degeneracies, can be obtained from EXAFS analysis and compared against different cluster models. As a proof of a principle, we have demonstrated earlier that this strategy can be used to solve the structure of both supported [2] and unsupported [3] clusters.

To compare EXAFS data for coordination numbers (n_i) against many possible structures of nanoparticles: regular and truncated polyhedra, a database of geometric properties of model clusters is needed. We wrote a suite of programs that generate x,y,z coordinates for most popular clusters structures and evaluate their pair radial distribution functions. Coordination numbers for several models (icosahedron, hexagonal closed packed (hcp), cuboctahedron and hemispherical, (111)-truncated cuboctahedron) are presented. This information can be directly compared with that obtained experimentally through EXAFS.

METHODS

Several geometrical characteristics of regular polyhedral clusters (e.g., the magic numbers, the number of atoms in specific positions, the number n_1 of nearest neighbor bonds) can be obtained analytically [4]. However, experimentally obtained (e.g., by EXAFS) n_1 number alone will not allow to discriminate, e.g., between the 55-atom icosahedral cluster model and 79-atom truncated octahedron cluster model since both will have $n_1 = 8.51$. Thus, higher order coordination numbers, which are time consuming to calculate analytically for each cluster geometry, are required to lift this “degeneracy”. Instead, we calculate the coordination numbers (n_1 through n_6) for any geometry by 1) generating cluster coordinates for regular many regular polyhedra, and 2) analyzing their pair radial distribution function.

Cluster Coordinates Generation

The suite of computer programs for an icosahedron, cuboctahedron (regular and truncated, with 111 and 100 planes), hcp, octahedron and truncated octahedron, was written in C++. Customized geometries (e.g., fcc bilayer or other asymmetric clusters) are also available. The input arguments are the desired order of the cluster (e.g., the number of atoms along the edge in a cuboctahedron or an icosahedron), and the nearest neighbor distance. The output generated is the table of x,y,z coordinates that is compatible for plotting with most molecular viewing programs (Fig. 1).

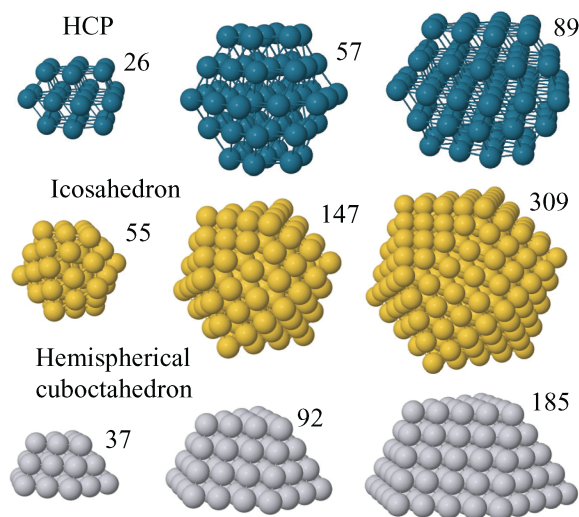


FIGURE 1. Atomic configurations and magic numbers for several characteristic clusters.

Pair Radial Distribution Function

For a cluster of N identical atoms, we can define cluster-average pair radial distribution function $\rho(r)$, or RDF, as follows:

$$\rho = \frac{\sum_{i=1}^N \rho_i}{N}; \quad \rho_i = \frac{dN_i}{dR_i} \quad (1)$$

where $\rho_i(r)$ is partial RDF for an atom i , and dN_i is the number of its neighbors within the spherical shell of thickness dR_i .

Coordination number within a given shell (between R_1 and R_2) can be obtained as:

$$n_i = \int_{R_1}^{R_2} \rho(r) dr \quad (2)$$

So defined, coordination numbers calculated in model clusters with Eq. (2) can be directly compared with those obtained by EXAFS. Indeed, if the integral in Eq. (2) is evaluated over the entire cluster: $R_1 = 0$, $R_2 = R_{\max}$, the result will be $N - 1$, which means that $\rho(r)$ (Eq. (1)) is properly normalized.

RESULTS

To demonstrate the role of the coordination numbers for the cluster geometry characterization, we plot the histogram of the RDF (bin size 0.05 Å) for an icosahedral and cuboctahedral clusters (Fig. 2).

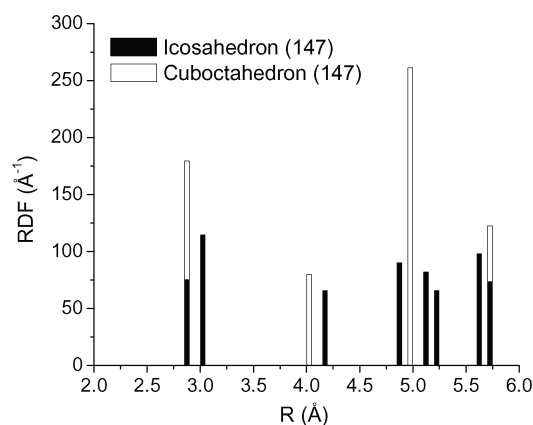


FIGURE 2. RDF histograms calculated for an icosahedron and a cuboctahedron. In both cases, $N=147$ and $R_1=2.87$ Å.

The 1NN distance was chosen to be 2.87 Å in both cases. Fig. 2 demonstrates the effect of the icosahedral strain (5%) on the n_1 through n_4 . Our recent STEM-EXAFS analysis of highly monodispersed, mixed-ligand Au₁₃ clusters [5] demonstrated the predictive power of this RDF method. Indeed, as shown in Tables 1 and 2, the index $n_2 = 0$ for a 13 atom icosahedron, while $n_2 = 1.85$ for a 13 atom cuboctahedron. Best fit (including multiple-scattering contributions) to the EXAFS data was consistent with the latter model. Thus, characteristic RDF signatures of different model clusters allowed us to unambiguously characterize the Au₁₃ clusters as icosahedral [5].

Figure 3 demonstrates that the higher order indices (n_2 through n_4) differ between these clusters throughout the large size range despite their identical magic numbers (Tables 1,2). Thus, accurate measurement of these indices in monodispersed clusters can allow to discriminate between the two different structures for larger clusters where the higher order neighbors are detectable by EXAFS.

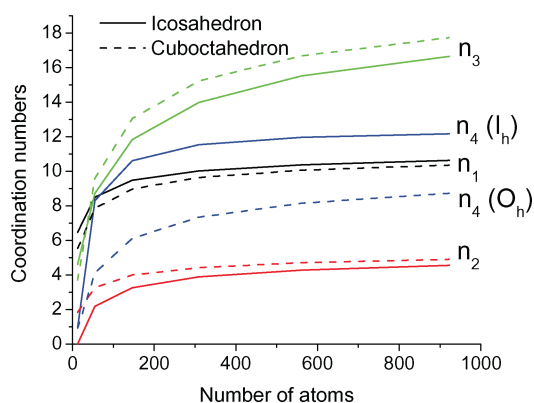


FIGURE 3. Coordination numbers n_1 through n_4 for icosahedron and cuboctahedron clusters.

Tables 1-4 below summarize the results for n_1 through n_6 in most commonly used clusters. The icosahedral splitting is amplified in the higher order shells and starts to overlap with adjacent shells, rendering EXAFS analysis impractical. By examining theoretical RDF in icosahedral clusters we find it impossible to experimentally resolve the structure at $r > 5$ Å. Thus, we report only n_1 through n_4 in Table 1.

TABLE 1. Coordination numbers for an icosahedron

N	n_1	n_2	n_3	n_4
13	6.46	0	4.62	0.9231
55	8.51	2.18	8.73	8.2909
147	9.47	3.27	11.84	10.61
309	10.02	3.89	13.98	11.53
561	10.37	4.28	15.51	11.96
923	10.62	4.55	16.64	12.17

TABLE 2. Coordination numbers for a cuboctahedron

N	n_1	n_2	n_3	n_4	n_5	n_6
13	5.54	1.85	3.69	0.92		
55	7.86	3.27	9.6	4.15	6.98	1.75
147	8.98	4	13.06	6.12	11.10	3.05
309	9.63	4.43	15.22	7.34	13.67	3.94
561	10.05	4.71	16.69	8.15	15.40	4.56
923	10.35	4.90	17.73	8.72	16.64	5.03

TABLE 3. Coordination numbers for an hcp cluster

N	n_1	n_2	n_3	n_4	n_5	n_6
13	5.54	1.85	0.46	2.77	0.92	0.46
26	6.92	2.31	0.54	5.77	1.85	1.85
57	8	3.16	0.91	7.58	4.63	2
89	8.56	3.51	0.97	9.03	5.12	2.76
153	9.10	3.92	1.16	10.12	6.51	3.10
214	9.42	4.09	1.21	11.02	6.84	3.53
323	9.73	4.35	1.33	11.70	7.65	3.73
421	9.93	4.48	1.35	12.29	7.87	4.01
587	10.14	4.64	1.43	12.76	8.40	4.14
732	10.28	4.72	1.46	13.17	8.56	4.33
967	10.42	4.84	1.51	13.51	8.94	4.42

TABLE 4. Coordination numbers for truncated octahedron

N	n_1	n_2	n_3	n_4	n_5	n_6
13	5.54	1.85	3.69	0.92		
38	7.58	2.68	8.84	3.16	5.05	1.47
79	8.51	3.19	11.54	5.01	7.90	2.43
140	9.09	3.56	13.37	6.17	9.94	3.14
225	9.49	3.84	14.72	6.99	11.52	3.70
338	9.80	4.07	15.76	7.60	12.78	4.14
483	10.04	4.25	16.60	8.08	13.81	4.51
664	10.23	4.40	17.28	8.46	14.68	4.81
885	10.39	4.53	17.84	8.77	15.40	5.06
1150	10.52	4.64	18.32	9.04	16.03	5.28

In summary, we analyzed many cluster geometries for their size, shape and structure study by EXAFS modeling. For analysis of multiple-scattering path degeneracies, or to study less common geometries, contact the authors: FRENKEL@BNL.GOV.

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