

New Growth Mechanism of Cubic Rh Clusters Composed of 8–12 Atoms Found by the Method of Euclidean Designs

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“Euclidean Design” a newly developed mathematical design theory has been used to reveal a heretofore hidden mechanism in the growth of cubic Rh clusters composed of eight to twelve atoms. This is the first application of this advanced mathematics to atomic cluster science as a powerful tool to optimize the geometrical structure. In the usual first principles calculation, initial structures have been given rather ad-hoc way by trial and error basis. The method proposed in the present paper is systematic and theoretically without any limitation on the number of atoms. For Rh clusters this report corrects the previously proposed structures [Y.-C. Bae, H. Osanai, V. Kumar and Y. Kawazoe: Phys. Rev. B **70** (2004) 195413], and shows that an eight atom cluster is a cube and that adding atoms on one side of the cubic cluster, growing to reach finally the two cube connected structure of a twelve atom Rh cluster. [doi:10.2320/matertrans.N-M2011859]

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1. Introduction

Bae *et al.*¹⁾ found a cubic structure for the ground state of a Rh cluster composed of eight atoms by the first principles calculation as a strange structure for metallic clusters, which have normally more compact form of Ih type. Although they also have computed and shown structures in more than eight atom cases, their result missed the systematic growth mechanism. It seems strange that only eight atom cluster is cubic and more than that there are no similar structures with this special property in their discovery. We have thought that there should be a series of better minimum geometric structures of the Rh cluster in which the cubic structure of eight atom does not stand alone. Up to the present, an initial structure for the first principles calculation in search of a stable atom cluster is given by guesses based on experience and it is likely that it does not always reach to the global minimum but to another local minimum. Some strategy is needed to discover a global minimum among many local minima and to understand the hidden growth mechanism of atom clusters. Different global optimization algorithms have been proposed and applied. For example, genetic algorithms was used to study the evolution of nano-particles, where the interactions between atoms, ions or molecules were described by a variety of potential energy functions.²⁾ K. Michaelian *et al.* applied *n*-body Gupta potential to explore the most stable isomers of nickel, silver and gold clusters.³⁾ In these algorithms, semi-empirical potentials are required. We have recently developed a geometrical method, (*Euclidean algorithm*), which is a suitable tool to generate discrete three dimensional coordinate points on multiple spheres having the same or different centers. This algorithm is applied to predict initial guess structures of unknown atomic clusters. By employing the Euclidean algorithm, we can, from a mathematical viewpoint, obtain natural and good configurations in a systematic way. For example, we can use it to find good configurations like regular polygons and Fullerene

C60.^{4,5)} By using this new mathematical technique, we have found a hidden mechanism which has never been recognized by the former try and error methods to find new cluster structures. We have generated initial structure based on the Euclidean algorithms, not by experience or common sense in cluster science. Using the first principles calculations, we have easily optimized these structures and found the better ground state geometries than those previously proposed. The present result shows that starting from the cubic eight atom Rh cluster, the growth starts to add atoms one by one reaching to the twelve atom cluster, which has a structure of combined two cubes. In between, nine atom cluster is composed simply one atom caps one side of the cube, ten atom cluster have two atoms on one side, and eleven atom cluster having three atoms on one side, and at last twelve atom cluster is composed of two connected cubes. This paper introduces a new mathematical method which might be useful to structural optimization in cluster science as a new guideline to generate initial structures before starting *ab initio* calculation trying to optimize the structure around the local minimum.

In Section 2 we will introduce the definition of Euclidean designs and describe the algorithms to obtain the coordinates of Euclidean designs. In Section 3 the computation results will be shown.

2. Mathematical Formulation

2.1 Euclidean design

In this section we introduce the notion of Euclidean designs, which is defined by Neumaier-Seidel⁶⁾ in 1988 in the mathematical design theory. First we describe some notation used throughout this paper. Let X be a finite subset in the d -dimensional Euclidean space \mathbb{R}^d . Let $\{r_1, r_2, \dots, r_p\}$ be the radii of concentric spheres on which elements of X lie. Let S_i denote the sphere of radius r_i centered at origin, and X_i denote the set of points in X which appear on S_i . σ_i denotes an $O(\mathbb{R}^d)$ -invariant measure on S_i where $O(\mathbb{R}^d)$ is the orthogonal group on \mathbb{R}^d and $|S_i|$ denotes the surface area of

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S_i . σ_i is unique up to a scalar multiplication. Also let w be a weight function on X and put $w(X_i) := \sum_{x \in X_i} w(x)$. Let $P_t(\mathbb{R}^d)$ be the vector space of polynomials of degree at most t in d variables over \mathbb{R} and $|X|, |X_i|$ be the numbers of points in X, X_i , respectively.

2.1.1 Definition II.1 (Neumaier-Seidel⁶⁾)

Under the above notation, (X, w) is a Euclidean t -design if for any $f(x) \in P_t(\mathbb{R}^d)$, the following equality holds:

$$\sum_{i=1}^p \frac{w(X_i)}{|S_i|} \int_{S_i} f(x) d\sigma_i(x) = \sum_{x \in X} w(x) f(x). \quad (1)$$

For example, let $w \equiv 1$ and

$$X_1 := \{(0, 0, 1), (0, 0, -1)\},$$

$$X_2 := \left\{ \left(-\frac{1}{\sqrt{3}}, 1, 0 \right), \left(-\frac{1}{\sqrt{3}}, -1, 0 \right), \left(\frac{2}{\sqrt{3}}, 0, 0 \right) \right\}.$$

Then $X = X_1 \cup X_2$ is a Euclidean 2-design on two concentric spheres.

2.2 Method

It is clear that X is a Euclidean t -design if and only if for all monomials of degree at most t , equality (1) holds. Denote by $M_t(\mathbb{R}^d)$ the set of monomials of degree t in d variables. For example, $M_1(\mathbb{R}^3) = \{x, y, z\}$, $M_2(\mathbb{R}^3) = \{x^2, y^2, z^2, xy, xz, yz\}$, $M_3(\mathbb{R}^3) = \{x^3, y^3, z^3, x^2y, x^2z, xy^2, y^2z, xz^2, yz^2, xyz\}$ and so on. Consider the following function:

$$X_1 = \{[0.37074, 0.37074, -0.85152], [-0.20120, -0.20120, -0.95866]\},$$

$$X_2 = \{[-0.04774, 1.18213, 0.20071], [-1.19974, 0.024197, -0.00472], [-0.11598, -0.11598, 1.18873], [1.18213, -0.047745, 0.20071], [0.02419, -1.19974, -0.0047]\}.$$

Here $G(X) = 0.16877$. Hence, to be exact, this is not a Euclidean 3-design, but we can say that it is close one to Euclidean design. This structure looks similar to 7a where the numbering follows¹⁾ and it is known that this structure has lowest energy among present-known ones with 7 rhodium atoms.

We can find Euclidean designs for arbitrary parameters $\{d, p, r_i, |X_i| \ (i = 1, \dots, p), t\}$ in the same way as the above example, and use them as the initial data to calculate structures with local minimum energy. In next section, we will show the computation results.

3. Results and Discussion

The density functional theory formalism is performed to study the structures of the Rh clusters with eight atoms to twelve atoms, by using Vienna *ab initio* simulation package (VASP).⁸⁻¹¹⁾ All atomic positions of the structures are fully relaxed until the maximum atomic force is less than 0.01 eV/Å. For the exchange–correlation functional, generalized gradient approximation PBE (GGA-PBE) is applied.^{12,13)} The cutoff energy is set to be 229 eV, and only Γ point is calculated for the Brillouin-zone integration. The energy is converged to an accuracy 1.0×10^{-5} eV. Since the occurrence of the magnetism in Rh clusters is confirmed by the experimental measurements in the temperature range from 60 to 200 K, spin polarization calculations are used.^{14,15)}

It was found by Y.-C. Bae *et al.* that the ground state of the Rh cluster with eight atoms (Rh₈) has the perfect cubic

$$G(X)$$

$$= \sum_{j=1}^t \sum_{f \in M_j(\mathbb{R}^d)} \left(\sum_{i=1}^p \frac{w(X_i)}{|S_i|} \int_{S_i} f(x) d\sigma_i(x) - \sum_{x \in X} w(x) f(x) \right)^2.$$

Here in the 3-dimensional case, $|S_i| = 4\pi r_i^2$, and for the polar coordinates system $x = (r_i \cos \theta \sin \phi, r_i \sin \theta \sin \phi, r_i \cos \phi)$, $0 \leq \phi \leq \pi$, $0 \leq \theta \leq 2\pi$, the invariant measure is given by $d\sigma_i(x) = r_i^2 \sin \phi d\phi d\theta$. By the above, X is a Euclidean design if and only if $G(X) = 0$. Euclidean designs do not necessarily exist for all parameters $d, t, |X|, \dots$. For example, there does not exist a Euclidean 4-design for a parameter $d = 2, p = 1, |X| \leq 4$ [refer to Ref. 7) about such lower bounds on the cardinality $|X|$ for the existence of Euclidean designs]. But we can always find what is very close to Euclidean designs as what minimizes $G(X)$. So we use such a configuration close to Euclidean design as the initial guess to search for a structure with lowest energy. For example it is known that cubic structure has lowest energy [refer Ref. 1)] and cube is a Euclidean 3-design on a sphere. The actual computation to find coordinates of designs was done by the software Maple.

2.2.1 Example

Put $d = 3, p = 2, r_1 = 1, r_2 = 1.2, t = 3, |X_1| = 2, |X_2| = 5, w \equiv 1$. $M_i(\mathbb{R}^3) \ (i = 1, 2, 3)$ is given by the above. Then carrying out the above minimization problem for $G(X)$ in an approximation, we obtain the following optimal configuration

structure.¹⁾ The energy of this ground state is 1.07 eV lower than any other stable structures. The ground state of Rh₉ is a capping of cubic Rh₈. But for the larger cluster, for example, Rh₁₀ and Rh₁₁, their structures are totally different from the cubic based structures. In their study, non-icosahedral growth was obtained. However, the relaxation of the cluster structures is strongly dependent on their initial geometrical structures, especially when two stable structures are separated by a high energy barrier. In our understanding, the initial structures mainly come from experimental results, experience, intuition and sometimes from a guess. The complexity increases with the number of atoms. Therefore, it is entirely possible to miss some possible stable structures. To search for the ground structures systematically, Euclidean designs are introduced into our present study. Euclidean designs are used to produce a series of prospective initial geometrical structures, then these structures are relaxed at the level of density functional theory.

The bulk of Rh is nonmagnetic material, however, in both clusters of atoms and monolayer films, the reduction of coordination number and higher symmetry enhance the magnetization. The magnetic momenta of clusters are dependent on the configurations.^{14,15)} To understand the growth mechanism of the Rh clusters, the clusters with eight atoms (Rh₈) to the clusters with twelve atoms (Rh₁₂) are studied. Three different initial guess structures are generated by applying Euclidean designs. These structures are relaxed until the criteria are satisfied. The relaxed structures are

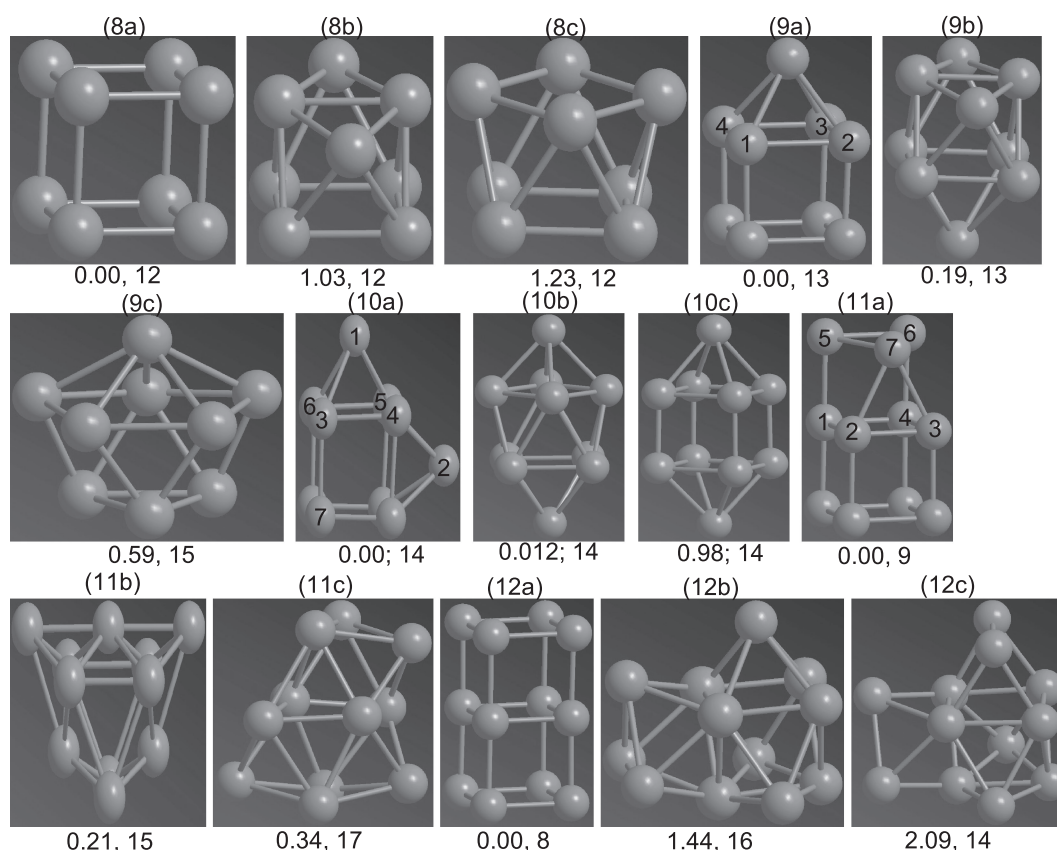


Fig. 1 Different atomic structures of Rh_8 to Rh_{12} clusters after relaxation. Isomer (a) has the lowest energy which is considered as the reference. The relative energies (eV) of other isomers and the corresponding magnetic moments (μ_B) are given below.

plotted in Fig. 1. It can be found that the ground state of Rh_8 clusters is closed to a perfect cube, which coincides with Y.-C. Bae's result. The average bond length is about 2.40 Å and the magnetic moment of this structure is $12\mu_B$. The geometrical structures, the energy differences and the magnetic moments of other stable states are shown in Fig. 1. Compared to the ground state, the magnetic moments are same but the total energy of the ground state is about 1 eV less than those of other structures. Three different relaxed Rh_9 clusters are obtained by the same method. The capped cube is the ground state. In this case, the cube is not the perfect cube. The bond lengths between the capped atoms and its four neighbors are about 2.55–2.56 Å. The capped atom can change the cubic lattice slightly. For example, the distance between atom 1 and atom 2 [shown in Fig. 1(9a)] is 2.54 Å and the distance between atom 1 and atom 4 is 2.44 Å. Both of them are longer than the bond length of the Rh_8 perfect cube. The growth mechanism from Rh_8 to Rh_9 can be understood. With one extra Rh atom approaching to one facet of Rh_8 cube, this atom can stay in the vertex position and form a square pyramidal structure with its four nearest neighbors. As reported by Y.-C. Bae, for the Rh_n cluster, this square pyramidal structure is ground state. However, the cubic base is very stable, and the extra atom can only change the cubic lattice slightly.

Rh_{10} is studied and the atomic structure of ground is depicted in Figs. 1(10a)–1(10c). It is found the neighboring bicapped cube (NBC) structure as shown in Fig. 1(10a) is the stable structure with the lowest energy. The cube is not a perfect one. For the perfect cube Rh_8 , the lattice is 2.4 Å for

each bond. However, for NBC structure, the bond length are different slightly. For example, the distance between atom 3 and atom 4 is about 2.5 Å, but the distance between atom 3 and atom 7 is very closed to the perfect cube. This means the existence of the capped atoms (atoms 1 and atom 2) reduce the interaction strength between the atoms in the cube. The atom 1 and the atom 3 to atom 6 form the square pyramid. The distance between atom 1 and its neighboring atoms are about 2.57 Å. NBC is a new structure which is not considered in Ref. 1), and Y.-C. Bae *et al.* reported that the ground structure of Rh_{10} was bicapped tetragonal antiprism (BTA) which is shown in Fig. 1(10b). Both of these structures are predicted by Euclidean design as the possible stable geometrical structures. BTA is relaxed and it is found that the total energy is about 0.013 eV greater than that of NBC. Since the energy difference is very closed to limitation of predicted properties by using DFT calculation, DMol³ is applied to confirm the result. In the calculation, double numerical plus diffusion (DND) basis set with pseudopotential VPSR and PBE exchange–correlation functional are used, and the result is almost same but the energy difference is around 0.01 eV. This suggest that NBC and BTA are nearly degenerate. It is already indicated in Ref. 1) that the ground state of Rh_9 cluster is capped cube. From the point view of cluster growth, it is interesting to realize that the NBC structure comes from the absorption of extra atom on the neighboring facet of Rh_9 cube. Actually, it is possible that the 10th atom is deposited on the opposite facet rather than the neighboring facet. This opposite capped cube is not predicted by Euclidean designs. To rule out this possibility, we relaxed this opposite capped

cube and its energy is 1 eV greater than the NBC structure. The conclusion that the occurrence probability of opposite capped cube is very low can be drawn. The magnetic moment of these two structures are $14 \mu_B$.

For eleven atom clusters, Euclidean designs predict 5 different prospective structures. These Rh_{11} clusters are relaxed, and three structures with the lowest energies are depicted. The ground state of Rh_{11} is shown in Fig. 1(11a). Interestingly, we can easily find that three atoms on the same side of the cube. The average length of the cubic lattice is about 2.4 \AA , which is equal to the lattice of cubic Rh_8 structure. Atom 5 and atom 6 are on the top of atom 1 and atom 4 respectively, the bond Rh_5-Rh_1 , the bond Rh_6-Rh_4 are 2.4 \AA approximately and the bond Rh_5-Rh_6 is 2.41 \AA . However atom 7 is in the bridge position and the distance between atom 2 and atom 7 is equal to the distance between atom 3 and atom 7. This cluster was not covered in Ref. 1), in their study, the energy of the fused pentagonal pyramids was the lowest. This fused pentagonal pyramids is predicted in Euclidean designs method. The geometry structure after relaxation is shown in Fig. 1(11b). The energy is about 0.2 eV greater than the cube based structure. Another surprising finding for the Rh_{11} clusters is that the magnetic moment of the fused pentagonal pyramids is $15 \mu_B$, which coincides with the Y.-C. Bae's result, but magnetic moment of cube based structure is only $9 \mu_B$. The reduced value satisfied with the experimental measurements.^{14,15} Finally, the ground state of Rh_{12} is shown in Figs. 1(12a)–1(12c). The fused cubes, whose magnetic moment is $8 \mu_B$, is found to be the state with the lowest energy. Compared with Rh_{12} and Rh_{11} , it is very easy to understand that the growth mechanism from Rh_{11} to Rh_{12} . It is cubic based growth as well. One extra atom approaches to the facet with three Rh atoms, and form two fused cubes. The average bond length is about 2.39 \AA , which is a little bit shorter than the perfect cube. The shorter bond length means that the interaction between Rh atoms becomes stronger and the corresponding structure is much more stable. The binding energies and the magnetic moment per atom of ground structure Rh_8 to Rh_{12} are calculated. The binding energy of Rh_n is defined as

$$E_b(Rh_n) = -(E(Rh_n) - n \times E(Rh))/n \quad (2)$$

where $E(Rh_n)$ is the total energy of structure Rh_n , and $E(Rh)$ is the energy of single Rh atom. The result is plotted in Fig. 2. From this figure, we find that with the increasing of the atomic number, the binding energies get greater and greater. The magnetic moment per atom decreases, with the atomic number increases. For Rh_{12} , the calculated result $0.67 \mu_B/\text{atom}$ is very closed to the experimental measurement $0.59 \pm 0.12 \mu_B$.

In this paper, a newly developed Euclidean designs are introduced to study the growth of Rh clusters. Our calculations show that the possible growth mechanism of Rh clusters is cube based from Rh_8 to Rh_{12} . Since the perfect cube structure is very stable, it is hard to change the structure significantly by adding one or several extra atoms. Therefore, the extra atoms can only form the bond with different facets of the cube. We speculate that the ground states of Rh_{4n} should be the fused cube. Also in this paper, we set the parameters as the weight constant and 2 concentric spheres.

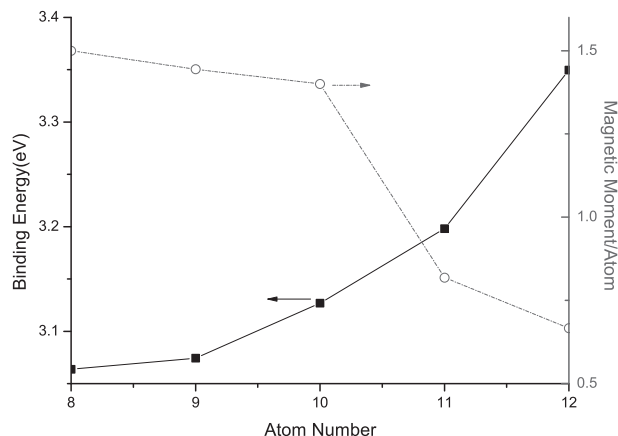


Fig. 2 The binding energy (black solid) and the magnetic moment per atom (dot-dashed).

The structures of Euclidean designs with the parameters include almost all present-known stable structures in the case of Rhodium metal clusters. Moreover, by using Euclidean designs, we can find new and more stable structures which were not listed in Bae *et al.* But from the definition of Euclidean designs, we can consider any weight on atoms and more than 2 concentric spheres. Also we do not need to limit the number of atoms when applying this algorithm. So the method could be applicable to other kinds of atoms without limitations to the number of atoms considered.

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