

Structures and its evolution of Ba_n ($n = 2 \sim 14$) clusters

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Abstract. We have studied the atomic structure and the electronic properties of Ba_n clusters by the *ab initio* molecular dynamics method. We find that a structural transition to the bulk-like structure begins at Ba_9 cluster, and the structures of the clusters are transferred to be icosahedral-like around $n = 13$. The relatively high stability for Ba_4 , Ba_{10} and Ba_{13} clusters are observed.

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1 Introduction

The experimental and theoretical studies of the atomic and molecular clusters have been an interesting subject. The research on the alkaline-earth cluster is of particular interesting, because it is a typical system to study how the physical properties changes as the size of the cluster increasing. Owing to the closed *s*-shell of the electronic configuration for the alkaline-earth atom, small clusters are expected to weakly bind with van der Waals bond while the binding in the bulk is metallic-like. This transition from van der Waals to metallic character in cluster has been one of the most challenging problem, which was studied in Be and Mg clusters [1–3] by using the first principles method. For Mg cluster, Kumar and Car found an oscillatory and slow convergence to the bulk metallic behavior. While in the Be cluster, Kawai and Weare found that bulk-like structural features for clusters having around 11 atoms and the *p* character of the electronic charge density is found to be close to its bulk value even for a 6-atom cluster.

The theoretical studies on Ba clusters are very much limited. There are some studies based on the jellium model [4] and the cylindrically averaged pseudopotential scheme [19], however the prediction of the ionization potential for Ba_n clusters provided by the jellium model is far from the recent experimental observations [5]. Very recently, Boutou *et al.* have studied Ba_n ($n = 2 \sim 6$) clusters with HF based method [6], and the structure of larger Ba_n clusters were studied by a model potential. They found that Ba_4 , Ba_7 and Ba_{13} clusters with a compact structure are very stable.

In this paper, by using the *ab initio* molecular dynamics method, we have obtained the ground state structure

of Ba_n clusters by fully optimizing a large number of initial structural configurations, and have studied the structural evolution from small clusters to large clusters. We find that the bulk-like structure of Ba_n cluster appears as early as $n = 9$.

2 Theoretical method

Our calculations are based on the density functional theory with a local density approximation [7–9]. The structures of clusters are optimized by the *ab initio* molecular dynamics method. The cluster is placed in a simple cubic cell with a lattice constant 18 Å. The size of the cell is large enough so that the interaction between a cluster and its periodic images is negligible. We have used the ultra soft pseudopotential [10–12] to describe the interaction between the valence electrons and the core. The wave functions are expanded in a plane wave base with an energy cutoff 83.0 eV. The exchange and correlation energy was calculated by the local density approximation [7] and GGA [13]. Only the Γ point is used in the summation of the Brillouin zone of the simulation cell.

Since we have no *a priori* knowledge as what structures of these clusters are, we have performed an extensive sampling of the potential surface by generating a large set of random structures as initial configurations for each cluster size n ($n = 2 \sim 14$). From each initial configuration, we optimize the structure by the conjugated gradient method, with a force convergence up to 0.02 eV/Å. Then we adopt the structure with the lowest binding energy as the ground state structure.

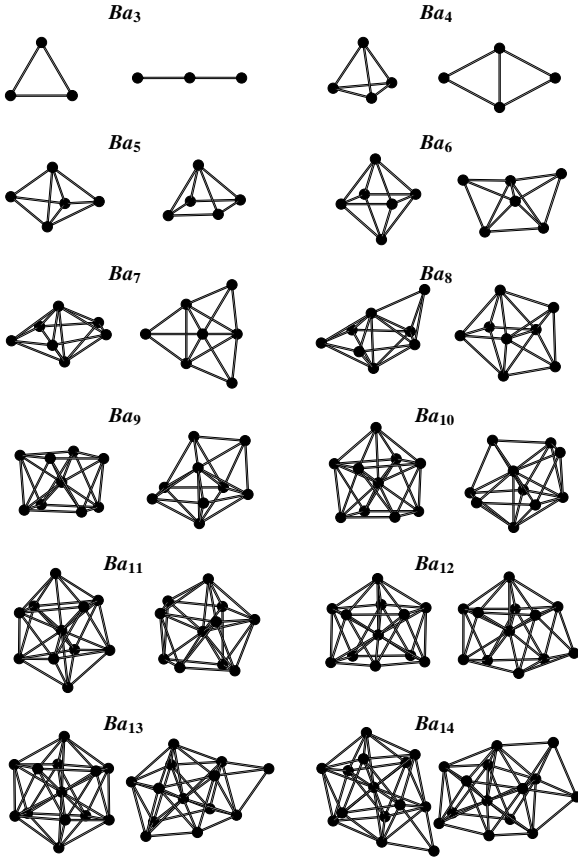


Fig. 1. The ground state structures and isomers of Ba_n ($n = 3 \sim 14$) clusters. For each cluster, the left is the ground state structure and the right is its isomer.

3 Results and discussions

3.1 Equilibrium structures and properties

We have optimized the structures of Ba_n ($n = 2 \sim 14$) clusters. The obtained equilibrium structures for $n = 3 \sim 14$ are shown in Fig. 1. For the comparison, their lowest isomers are also presented. The binding energies of the structures and their symmetries are presented in Table 1. Ba_2 dimer was investigated previously in a rather elaborated CI method [14]. We find that the equilibrium distance and the cohesive energy of Ba_2 are 4.96 Å and 0.243 eV respectively, which are 1.6% and 20% larger than CI results [14]. Given that LDA usually overestimates cohesive energy, our data are in close agreement with CI results, which suggests that the present method can be used to correctly describe Ba clusters.

The structures of $Ba_3 \sim Ba_5$ clusters are triangle-like or tetragonal-like compact structure, as observed in many other metal clusters. The lowest structure of Ba_3 is an equilateral triangle, whose binding energy is about 0.2 eV lower than its lowest isomer with a linear structure. The structure of Ba_4 is a compact tetrahedron, while its isomer is still a planar rhombic structure, which indicates that the

Table 1. The symmetry and the binding energy per atom (eV). Only those structures plotted in Fig. 1 are presented.

Size n	Equilibrium	Structure	Isomer	Structure
	<i>Symmetry</i>	E_b/n	<i>Symmetry</i>	E_b/n
2	Linear	0.1215	-	-
3	D_{3h}	0.3637	Linear	0.1378
4	T_d	0.6097	D_{2h}	0.4818
5	D_{3h}	0.7352	D_4	0.6943
6	D_{4h}	0.7953	C_{2v}	0.7900
7	D_{5h}	0.9118	C_{3v}	0.8382
8	C_s	0.9342	C_{2v}	0.9191
9	C_{4v}	1.0040	C_{2v}	0.9966
10	C_{4v}	1.0788	C_{3v}	1.0415
11	C_{4v}	1.1023	C_{2v}	1.0999
12	D_{5h}	1.1462	C_1	1.1228
13	D_{5h}	1.2343	C_s	1.1431
14	C_{3v}	1.2155	C_{2v}	1.1651

transition from planar to three dimensional structure begins. From Ba_6 , the regular tetrahedron based structure are not the ground state structure even more. The ground state structures for Ba_6 and Ba_7 are a regular octahedron and a pentagonal biyramid, respectively. While the tetrahedron based structures (see Fig. 1) are their isomers. The ground state structure of Ba_8 can be considered as an atom capped on the pentagonal biyramid of Ba_7 . These results are in good agreement with what obtained by HF based method [6], except that a small difference for structure of the Ba_6 cluster.

The structure transition to the bulk-like structure takes place Ba_9 cluster. We find that the ground state structure of Ba_9 is a slightly deformed cubic, *i.e.*, the unit cell of Ba solid phase with BCC structure. The structures of Ba_{10} and Ba_{11} are one or two atoms capped on the surfaces of the cubic respectively, while the capped pentagonal biyramid structures are all the isomers. We have also studied other possible structures for Ba_9 , such as tricapped trigonal prism observed in Mg_9 cluster [2]. We find that the cubic-like structure shown in Fig. 1 is truly the ground state for Ba_9 . For example, the tricapped trigonal prism, which is the ground state structure of Mg_9 , is about 0.79 eV higher in energy.

We find that Ba_{13} cluster shows a deformed icosahedral structure, structures of Ba_{12} and Ba_{14} can be obtained by removing one atom from the icosahedron or capping one atom on the icosahedron. It is interesting to note that, the isomers for these clusters are also icosahedral-like structures, which strongly suggests that the icosahedral structures dominate the the potential surface of Ba cluster around $n = 13$.

To quantitatively look into the structures of Ba clusters, we have calculated the average interatomic bond length and the average coordination number in a cluster

defined as below:

$$\langle R \rangle = \frac{1}{N} \sum_{i,j} R_{ij} \quad (1)$$

$$C_n = \frac{1}{n} \sum_i C_i \quad (2)$$

where R_{ij} is the interatomic bond length between the i th atom and its neighbor j atom, N is the count number of R_{ij} . C_i is the coordination number of the i th atom, n is the number of atom in the cluster. We consider an atom j to be the neighbor of atom i if the distance R_{ij} is smaller than a cutoff 5.22 Å, 20% longer than the bond length in bulk.

The obtained results are shown in Fig. 2. We find that the average interatomic bond length of Ba clusters converges to ~ 4.3 Å quickly, very close to the theoretical bond length in the bulk phase. Two dips at $n = 6$ and $n = 9$ reflects the different symmetry of the structure. Comparison with the results obtained for Mg cluster [2], the convergence of the interatomic bond length is much faster. However, the average coordination number is far from convergence, since in these small clusters most of the atoms are still on the surface with lower coordination number. To describe how the average coordination number Z_T changes with size of the cluster, we propose an empirical formula based on the formula given by Bhatt *et al.* [15]:

$$Z_T(n) = \frac{n-1}{1+\alpha \times (n-1)} \quad (3)$$

where α is a parameters. Z_T should be 8 at close-packed density. As to our results, we chose α as a constant, 0.0684. From the lower panel of Fig. 2, we can see that it could fit the calculated data properly.

3.2 Electronic properties

In order to further study how the physical properties of Ba clusters changes as the size of the cluster increasing, we have studied the electronic structures of the clusters. We have calculated the s , p and d electrons of Ba atom in cluster by projecting the valence charge in the Wigner-Size sphere (2.08 Å) into atomic orbitals. Although the space division is somewhat arbitrary, the obtained results can qualitatively provide the information on the electronic structures of the cluster which are shown in Fig. 3. As we can see that, the number of electrons changes very quickly from Ba₂ to Ba₅, the delocalized s electrons decrease significantly and the p and d electrons increase. Starting from $n = 9$, the number of electrons for all s , p and d orbitals almost saturates and converges to a constant, which indicates that a structural transition occurs at Ba₉ in agreement with the results obtained from atomic structure.

The monotonical increase of calculated binding energies for Ba_n clusters, shown in Fig. 4, suggests that energy

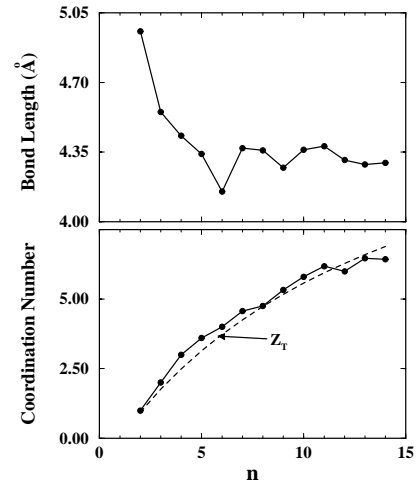


Fig. 2. Upper panel: the average interatomic bond length as a function of cluster size. Those clusters corresponding to the structure transitions, such as Ba₆, and Ba₉, have short average interatomic bond length. Lower panel: the average coordination number as a function of the cluster size. Dashed line is for our empirical formula (Z_T), which could properly fit the calculated values.

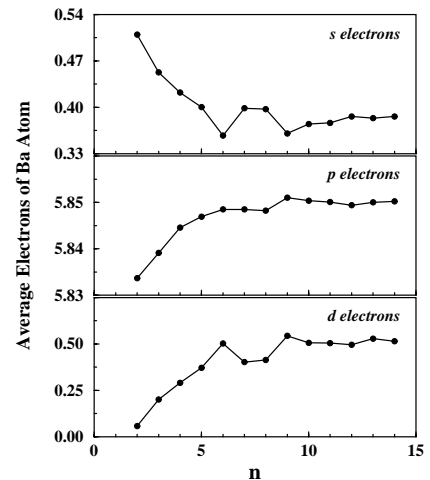


Fig. 3. The average s , p and d electrons in Ba_n clusters projected from the valence charge. The saturations of the projected electrons at $n = 9$ suggests that a transition occurs.

convergence to bulk behavior is slow in these small clusters in which the surface effect will be still important. To study the stability of Ba_n clusters in more details, we calculated the second order finite difference of binding energy Δ_2 and the dissociation energy E_n^{diss} as a function of the cluster size n , which are defined as:

$$\Delta_2(n) = E_{n+1} - 2E_n + E_{n-1} \quad (4)$$

$$E_n^{diss} = E_{n-1} + E_1 - E_n. \quad (5)$$

The second order finite difference of total energy is a general measure of the relative stability. Dissociation energy is

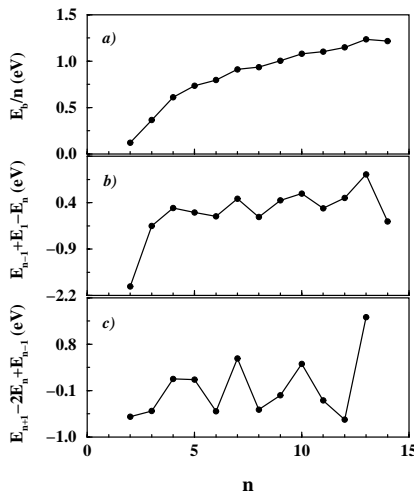


Fig. 4. The average binding energy per atom (a), dissociation energy for the monomer E_n^{diss} (b), second order finite difference of total energy Δ_2 (c). Ba_4 , Ba_{10} and Ba_{13} show a higher stability.

the energy required to evaporate an atom from the cluster, which is useful to examine the stability as well. Combining the results shown in Fig. 4b and Fig. 4c, we can find that Ba_4 , Ba_{10} and Ba_{13} clusters have higher stability. It is easy to understand why Ba_{13} cluster shows a high stability, the geometry of the close pack structure will be an important reason. In fact the high stability of the regular icosahedron structure has been observed in many other metallic clusters. It would also not surprise to find that Ba_4 cluster with tetrahedron structure, which is also the most compact structure, shows a high stability. However, one can not attribute the high stability of Ba_{10} cluster as the geometry effect, since its structure obtained in our calculation is obviously not the most compact one. The high stability of Ba_{10} can be explained by its electronic effects. Since Ba_{10} cluster has 20 valence electrons, according to the spherical jellium model [16–18], it can fill up to a close shell which would lead to a high stability of Ba_{10} cluster.

In summary, by using the *ab initio* molecular-dynamics method, we have studied the structural and electronic properties of Ba_n clusters. For the smaller Ba cluster, our obtained ground state structures are in agreement with previous HF based calculation [6], but significant difference in the ground state structure has been observed between our present *ab initio* results and model potential results in the larger Ba cluster ($n > 6$). We find that,

the structural transition to the bulk-like structure appears as early as $n = 9$, however, the icosahedral-like structures dominate Ba_n cluster around $n = 13$ as in many other metallic clusters. The number of the projected electrons shows that the electronic structures almost converges starting from $n = 9$. The high stability of Ba_4 , Ba_{10} and Ba_{13} have been observed and explained according to the geometric effects and electronic effects.

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