Stability and bonding nature for icosahedral or planar cluster of hydrogenated boron or aluminum

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ABSTRACT

Ab initio molecular orbital calculations are performed for $B_{13}^-$, $Al_{13}^-$, $B_{12}H_{12}^-$, $Al_{12}H_{12}^-$, $Si_{10}^-$, and $Si_{10}H_{16}$ clusters. The highest occupied molecular orbital (HOMO) of stable and unstable clusters is bonding and antibonding orbitals, respectively. The cluster size dependences of the orbital energies are almost the same for $B_{13}^-$ and $Al_{13}^-$ icosahedral clusters, when the size and the energy are properly normalized. The normalized factors for size and energy are almost coincident with the ratios of those of the atomic outer s orbitals. On the other hand, the most stable size of $B_{11}^-$ is smaller than that of $Al_{13}^-$, and this ratio of the stable size seems to be affected by the ratio of the sizes of the atomic outer p orbitals. As a result, $B_{13}^-$ and $Al_{13}^-$ icosahedral clusters have antibonding and bonding orbitals for HOMOs and so are unstable and stable, respectively. The situation for $B_{13}^-$ and $Al_{13}^-$ planar clusters is opposite to that discussed above for the icosahedral clusters. The orbital energies for the metallic bonding $Al_{13}^-$ icosahedral and $Si_{10}^-$ clusters can be reproduced by the Woods–Saxon model; however, those for the unstable $B_{13}^-$ icosahedral and covalent bonding $B_{12}H_{12}^-$, $Al_{12}H_{12}^-$, and $Si_{10}H_{16}$ clusters cannot be reproduced by the Woods–Saxon model. After optimization of the parameters of the Woods–Saxon model for the $Al_{13}^-$ icosahedral and $Si_{10}^-$ clusters, the orbital energies are reproduced very well and the sizes and shapes of the potential are reasonable.

I. INTRODUCTION

A cluster is a group of a countable number of atoms. The cluster has an interesting nature and a structure that is different from the bulk solid or an isolated atom or molecule because of the special cluster size. Many computational studies have been performed to predict the properties of clusters, and it has been proposed that films with new functions may be obtained by controlling the structure of clusters. A Si cluster with a transition metal atom and a boron hydride cluster as a boron dopant are examples of structurally controlled clusters. The boron hydride cluster also has other uses because it changes its stable structure depending on the degree of hydrogenation. A boron hydride cluster $B_nH_m$ has an icosahedral structure, as observed in a boron crystal, but a boron cluster $B_n$ has a planar structure. The planar structure is expected to construct a plane with a graphene-like structure that has a hexagonal and triangular lattice. The aluminum hydride crystal ($AlH_3$) is promising as a hydrogen storage material because it can contain up...
to 10.1 wt. % of H atoms. However, Al crystals hardly react with H₂ at normal temperature and pressure. This problem can be solved by using an Al cluster because the energy barrier of the physical hydrogen adsorption reaction of an Al cluster is smaller than that of an Al crystal. Investigations using density functional theory (DFT) calculations have revealed that more Al or B atoms contained in the cluster will result in a lower energy barrier. BₙHₘ releases molecular BₓHᵧ when it adsorbs more hydrogen than the amount expressed by the Wade law. The cluster, as a building block, is useful to understand the properties of a crystal. Quasicrystals and their approximants are examples of cluster solids, for example, one containing an icosahedral Al₁₂ cluster. In such a solid, the Al₁₂ cluster converts its bonding nature without changing the icosahedral structure. Al₁₂ clusters with a rhenium (Re) atom at their center have a metallic bond and those without a Re atom have a covalent bond. This bonding conversion changes the electrical property of the whole bulk solid. B is a group-13 element, the same as Al, and there exists an icosahedral B₁₂ cluster in a boron crystal. Different from Al, other atoms are not located at the center of the cluster, but the B crystal changes the covalent bond to a metallic bond by the vanadium atom being doped in another site. All of these bonding conversions are caused without collapsing the icosahedral cluster structure.

Isolated clusters change the metallic bond to a covalent bond by hydrogenation. A Si₁₀ cluster has a metallic bond, and its structure is compact, but hydrogenated Si₁₀H₄ has a covalent bond, and it forms a diamondlike structure. Although Al and B belong to the same group in the periodic table, the bonding nature and stable structure of isolated Al and B clusters are different. An Al cluster changes the metallic bond to a covalent bond by hydrogenation with the same icosahedral structure [Figs. 1(a)–1(c)]. On the other hand, the B cluster forms a planar structure [Fig. 1(b)], and the structure is changed from planar to icosahedral by hydrogenation [Fig. 1(c)]. It is proposed that the bonding conversion is a π bond to σ bond. Typically, it is known that a cluster with a specific number of atoms or valence electrons is more stable than other clusters, and this special number is called the magic number. The magic number depends on the geometric shell model like a rare gas cluster, the electronic shell model like an alkali metal cluster, or the stability of molecular bonding like a fullerene. For a metallic bond cluster, the Woods–Saxon model can be applied. The Woods–Saxon model is a kind of free electron approximation. In this model, the cluster shape is approximated to a sphere and the valence electrons are influenced by the interface of the cluster. As shown in Fig. 2, as an intermediate model between a harmonic oscillator and a square well, the potential for the electron can be expressed as

\[ V\left[ \frac{1}{1 + \exp\left( \frac{r - R}{a} \right)} \right]^{-1}. \]  

Here, \( r \) is the distance from the center of the cluster, \( R \) is the radius of the cluster, \( V \) is the depth of the potential, and \( a \) is the diffuse parameter which corresponds to smoothness at the boundary of the cluster. The magic numbers of valence electrons calculated using this model are 2, 8, 18, 20, 34, 40, 58, 78, . . . . When a cluster follows this model, the orbital energy levels can be classified as 1s, 1p, 1d, 2s, 2p, 1f, . . . , by the orbital structure and degeneracy, like an atom. If the number of valence electrons in the cluster is one of the magic numbers, the cluster becomes closed shell and electronically stable. For example, a Na₆ cluster is a typical metallic bonding cluster, and it follows this model well. Hence, in a metallic bonding cluster, valence electrons can be approximated as free electrons. In other words, when the orbital level follows this model well, the bonding condition of the cluster can be judged to be a metallic bond. An Al₁₃⁺ cluster has 40 valence electrons, and 40 is the magic number for occupying up to a 2p orbital, so it is very stable. Al₁₃⁻ is also geometrically stable because it forms an icosahedral structure with a center atom [Fig. 1(a)]. According to these two reasons, an Al₁₃⁻ cluster is more chemically stable than other Al clusters, and it hardly reacts with oxygen, whereas the others do react with oxygen. However, B₁₃⁻ forms a planar structure [Fig. 1(b)] and when in an icosahedral structure [Fig. 1(a)], it is unstable, not even with a locally stable structure.

In this paper, we investigate B₁₃⁻, Al₁₃⁻, B₁₂H₁₂²⁻, Al₁₃H₁₂²⁻, Si₁₀, and Si₁₀H₁₆ clusters. To clarify the contribution of the cluster orbital to the structural stability, we investigated the orbital energies as a function of the radius of the clusters. We also examined the dependence of the structural stability on whether the highest occupied energy orbital (HOMO) is bonding or antibonding. Finally, we compared the energy levels of the clusters with those of the
Woods–Saxon model to judge if the cluster has metallic bonding or not.

II. CALCULATION METHOD

We calculated the cluster structure and orbital energy using Gaussian 03W and Gaussian 09W based on density functional theory (DFT). To investigate whether the B3LYP functional can be used for the hydrogenated Al cluster, we calculated the bonding energy and wavenumber of the Al–H molecule using 9 functionals at the 6-31g(d) level and compared the results of the calculation and experiments. To optimize the three structures (ICOSAHEDRON, PLANE, and CAGE), stable structures of Al_{13}^− (ICOSAHEDRON), B_{13}^− (PLANE), Al_{12}H_{12}^− (CAGE), and B_{12}H_{12}^− (CAGE) were optimized, and Si_{10} and Si_{10}H_{16} were optimized. Structures of the unstable Al_{13}^− (PLANE) and B_{13}^− (ICOSAHEDRON) were optimized in two steps. First, the initial structure was applied to the optimized PLANE for the B_{13}^− or ICOSAHEDRON for the Al_{13}^− structures. Next, the bond lengths were optimized by fixing the bonding angles when the total energy was minimized.

We also calculated the cluster radius dependence of the orbital energies by fixing the bond angle. Here, the Al_{13}^−, B_{13}^−, and Si_{10} clusters have 40 electrons, which is one of the magic numbers for a metallic bonding cluster. The hydrogenated clusters Al_{12}H_{12}^− and B_{12}H_{12}^− have 50 electrons, and Si_{10}H_{16} has 56. These are not magic numbers.

III. DETERMINATION OF A SUITABLE FUNCTIONAL FOR THE CLUSTERS

It was determined that the most suitable functional for the optimization of a boron hydride cluster was B3LYP. Experimentally, the binding energy of the Al–H bond, infrared absorption spectra, and ionization energy (IE) of Al_{n} were determined. To determine if the B3LYP functional could be applied for the aluminum hydride cluster, we calculated the AlH molecule using the generalized gradient approximation (GGA) functionals BLYP, PW91, BPBE, PBE, TPSS, B3LYP, B3PW91, PPBE0, and TPSSH at the 6-31g(d,p) level. We compared the calculated results and experimental values of the binding energy and the vibrational wavenumber of Al–H. The value of the binding energy of Al–H calculated with B3LYP was within the range of the error of the experimental values (Fig. 3). The value of the calculated vibrational wavenumber slightly deviated from the experimental range (Fig. 4). The structure of Al_{n} (n = 1–13) was optimized in each functional, and the vertical ionization energy (vIE) (eV) was calculated as the energy difference between Al_{n} and Al_{n}^+, which was then compared with that determined by experiment. The value for each n is shown in Fig. 5, and the average of the absolute error for the B3LYP functional was the lowest. Therefore, by considering the reproducibility of the Al–H bond and Al_{n} clusters, it was confirmed that B3LYP can be used for aluminum hydride clusters. A similar accuracy can be expected for Si clusters.
IV. RELATION AMONG BONDING NATURE OF HOMO, RADIUS OF ATOMIC ORBITAL, AND STRUCTURAL STABILITY OF CLUSTER

Each valence orbital of the clusters can be classified by their atomic-orbital-like shape and degeneracy. For example, the molecular orbitals of Al$_{13}^-$ (ICOSAHEDRON), B$_{13}^-$ (ICOSAHEDRON), Al$_{12}$H$_{12}^-$ (CAGE), and B$_{12}$H$_{12}^-$ (CAGE) can be classified as 1s, 1p, 1d, 2s, 1fa, 1fb, 2p, 1ga. . . [Fig. 6(a)]. Orbital f is degenerated in 7 and g in 9, but they are resolved in 1fa and 1fb, and in 1ga and 1gb, respectively, because both ICOSAHEDRON and CAGE clusters have icosahedral symmetry [Fig. 6(a)]. Al$_{13}^-$ (ICOSAHEDRON) and B$_{13}^-$ (ICOSAHEDRON) have 40 electrons, and the occupied orbitals are 1s, 1p, 1d, 2s, 1fa, 1fb, and 2p. Al$_{12}$H$_{12}^-$ (CAGE) and B$_{12}$H$_{12}^-$ (CAGE) have 50 electrons, and 25 orbitals (1s to 1ga) are occupied. B$_{13}^-$ (PLANE) and Al$_{13}^-$ (PLANE) could not be compared with other clusters because they were far from spherical. Therefore, each occupied orbital of the planar clusters was named from one for the lowest energy orbital in sequence in B$_{13}^-$ (PLANE) [Fig. 6(b)]. Because the B$_{13}^-$ (PLANE) and Al$_{13}^-$ (PLANE) orbitals, being the same shape, were named in the same number, the sequence of number interchanged somewhere in Al$_{13}^-$ (PLANE). So the number of the HOMO of B$_{13}^-$ (PLANE) was 20, and that of the lowest unoccupied molecular orbital (LUMO) was 21. The number of the HOMO of Al$_{13}^-$ (PLANE) was 25, and that of the LUMO was 20. Si$_{10}$ and Si$_{10}$H$_{16}$ were different from an icosahedron, and their orbitals were resolved as less spherical than of ICOSAHEDRON or CAGE, but they could also be classified as spherical clusters [Figs. 6(c) and 6(d)].

As for all clusters, the cluster size when the total energy is minimized is called the most stable size. The sizes refer to the distances between atoms other than H and the cluster center of ICOSAHEDRON and CAGE, or an average of nearest neighbor atomic distances other than those to H of the other clusters. Lengths of B–H, Al–H, and Si–H were fixed at those of the most stable size cluster. The relationships between the cluster size and orbital energy are shown in Fig. 7. Most of the occupied orbitals (solid lines) were the bonding orbitals, the energies of which decreased with decreasing the cluster size. On the other hand, most of the unoccupied orbitals (broken lines) were the antibonding orbitals.

From the total energy $-29.18$ eV for Al$_{13}^-$ (ICOSAHEDRON) and $-25.11$ eV for Al$_{13}^-$ (PLANE), ICOSAHEDRON is more stable than PLANE for Al. On the other hand, from the total energy $-51.87$ eV for B$_{13}^-$ (ICOSAHEDRON) and $-63.21$ eV for B$_{13}^-$ (PLANE), PLANE is more stable than ICOSAHEDRON for B. These results are consistent with those described in the Introduction.

As shown in Fig. 7(a), the most stable size of stable Al$_{13}^-$ (ICOSAHEDRON) is located at the right of the cross point of the 1fa and 2p orbitals; therefore, the HOMO is a bonding orbital. On the other hand, that of the unstable B$_{13}^-$ (ICOSAHEDRON) is located at the left of the cross point, so the HOMO is an antibonding orbital. Planar clusters have a similar situation. B$_{13}^-$ (PLANE) is a stable cluster, and its HOMO is a bonding orbital. On the other hand, the HOMO of the unstable Al$_{13}^-$ (PLANE) is antibonding because the stable size of the Al$_{13}^-$ is larger and the energy of the lowest antibonding orbital becomes lower than that of the highest bonding orbital. These results show that the stable structure and the stable size of the cluster are clearly different between Al and B although Al and B belong to the same group in the periodic table. For the unstable Al$_{13}^-$ (PLANE), there are some cluster sizes where the orbital shapes exchange and almost the vertical lines are connecting the orbital energies which have the same shapes. These exchanges may be the results of the energy gap induced by the interaction between two orbitals which have the same symmetry and the same energy.

Figure 7(b) shows that both HOMOs of stable B$_{12}$H$_{12}^-$ (CAGE) and stable Al$_{12}$H$_{12}^-$ (CAGE) are bonding although the
most stable sizes of the former and the latter are located at the left and the right of the cross point of the 1fa and 2s orbitals, respectively. However, although the size dependence of the energy levels is similar, the relative positions of the most stable size are different. The case of the silicon cluster is shown in Fig. 7(c). The HOMOs of both stable Si\(_{10}\) and Si\(_{10}H_{16}\) are bonding orbitals. For all cases investigated in this work, the HOMO of stable clusters was bonding, but the HOMO of unstable clusters was antibonding around the most stable size. Therefore, the most stable structure of each cluster seems to be determined by whether the HOMO is bonding or antibonding.

Focusing on B and Al clusters with the same structure, the relationships between the cluster size and orbital energy exhibited a similar tendency, but the positions of the most stable size were smaller and larger for B and Al, respectively. As for Al\(_{13}\)\(^{-}\) (ICOSAHEDRON) and B\(_{13}\)\(^{-}\) (ICOSAHEDRON), the size dependences of the orbital energy of each cluster showed a similar tendency, but the most stable size of Al\(_{13}\)\(^{-}\) (ICOSAHEDRON) was located at the longer side of the cross point and that of B\(_{13}\)\(^{-}\) (ICOSAHEDRON) at the shorter side. It seems that this difference originated from the size difference of the B and Al atomic orbitals. We normalized the two axes of B\(_{13}\)\(^{-}\) (ICOSAHEDRON) and Al\(_{13}\)\(^{-}\) (ICOSAHEDRON), that is, the energy and size axes for B were reduced and expanded, respectively, as the cross point of the 1fb and 2p orbitals and each line overlapped as much as possible (Fig. 8). Table I shows some values for the energies and sizes of the B and Al atomic orbitals and clusters. Both the ratios of the energy levels and radii of the B\(_{13}\)\(^{-}\) and Al\(_{13}\)\(^{-}\) clusters were near the ratios of the atomic s orbital.
FIG. 8. Two axes of ICOSAHEDRON in Fig. 7(a) are normalized, that is, energy and size axes for B are reduced and expanded, respectively, as the cross points between 1p and 2p orbitals coincide at the same position and each line overlaps as much as possible. The blue line shows B$_{13}^-$, and the red line shows Al$_{13}^-$. Vertical lines show the most stable size of B$_{13}^-$ and Al$_{13}^-$. Energies and the radii of B and Al (italic numbers in Table I), respectively. The ratio of the cluster orbital energy to radius seemed to be strongly dependent on the atomic s orbitals. On the other hand, the ratio of the cluster radii of the most stable size was sufficiently larger than the above value, and it was considered to be influenced by the ratio of the sizes of the p atomic orbitals (bold numbers in Table I). Although the radii of the atomic orbitals of 2s and 2p for B were near, the radius of 3p was larger than that of 3s for Al because the 2p orbital does not have 1p in the inner shell, but 3p has 2p in the inner shell and should be pushed out. The stable sizes of the Al clusters, Al$_{13}^-$ (ICOSAHEDRON), Al$_{13}^-$ (PLANE), and Al$_{12}H_{12}^2$ (CAGE), were considered to be affected by this pushing out of the atomic 3p orbital.

FIG. 9. Comparisons of metallic and covalent bonds, and metal and nonmetallic materials.

TABLE I. Values for energies and sizes of B and Al atomic orbitals and clusters. [a] was calculated in this work. Italic values show almost the same values for energy and size, respectively. Boldface values are different from italic values and are related with each other.

| Energy                  | B       | Al     | Al/B   |
|-------------------------|---------|--------|--------|
| Ionization energy (eV)  | 8.298   | 5.986  | 0.721  |
| Atomic orbital energy (eV) |        |        |        |
| s (B 2s, Al 3s)         | −10.37  | −8.684 | 0.869  |
| p (B 2p, Al 3p)         | −4.677  | −3.572 | 0.764  |

| Ratio of orbital energies of B$_{13}^-$ and Al$_{13}^-$ clusters | 0.86 |
|---------------------------------------------------------------|-----|

| Size                     | B       | Al     | Al/B   |
|--------------------------|---------|--------|--------|
| Radius of atomic orbital (Å) |        |        |        |
| s (B 2s, Al 3s)          | 0.769   | 1.044  | 1.36   |
| p (B 2p, Al 3p)          | 0.776   | 1.312  | 1.69   |
| X$_2$ bond length (X = B, Al, Å) [a] | 1.641 | 2.56   | 1.55   |
| Stable cluster size (Å) [a] | 1.776  | 2.68   | 1.51   |
| Ratio of size (radii) of B$_{13}^-$ and Al$_{13}^-$ clusters | 1.4   |
V. VALIDITY OF THE WOODS–SAXON MODEL FOR METALLIC BOND OF CLUSTER

The words “metal” and “metallic bond” are often confused, so we first define these in Fig. 9. Metal elements become stable ions by releasing a few electrons. These electrons (valence electrons) spread through the whole system, and the system gets cohesive energy because the kinetic energy of the electrons decreases. These ions and electrons condense owing to the Coulomb attraction. This is the condensing mechanism for metal solids. Metal atoms in metallic bonding clusters can be estimated to bond with the same mechanism. In a metallic bonding solid, the valence electron behaves as a free electron and it becomes a metal. A metal is a solid whose density of state \( D(\varepsilon) \) at the Fermi energy \( \varepsilon_F \) is finite and the wave function at \( \varepsilon_F \) is extended; therefore, the electrical conductivity is not zero even at a temperature of absolute zero. On the other hand, when \( D(\varepsilon_F) \) is zero or the wave function at \( \varepsilon_F \) is localized, the solid becomes nonmetallic, that is, an insulator or semiconductor. Focusing on a cluster, it has very few atoms and the energy level is not continuous. Accordingly, a cluster cannot be a metal even when the HOMO is not perfectly occupied. However, the bonding of a cluster can be metallic when the valence electrons behave as free electrons in the empty sphere space, which has the same size as the cluster, that is, the valence electron system can be described by the Woods–Saxon model. In short, energy levels of cluster orbitals correspond to those of the model when the cluster has a metallic bond.

We calculated the orbital energy level of each cluster and compared it with the eigen energy level of the Woods–Saxon model [Figs. 10(a) and 10(b)]. The lines on the left side refer to the energy levels of the Woods–Saxon model, and the lines on the right side refer to the calculated orbital energy levels of each cluster. The left side is normalized as the heights of the 1s and 2p lines become the same as those on the right side. It is possible to compare only the order of the orbital energies.

Al\(_{13}^-\) (ICOSAHEDRON) and Si\(_{10}\), which have a metallic bond follow the Woods–Saxon model. The HOMO of Al\(_{13}^-\) (ICOSAHEDRON) is a 1fb orbital, and its energy is higher than that of the 2p orbital, but the order of the orbital energy is not interchanged because these two orbitals have almost the same energy. The 1d and 1f orbitals of Si\(_{10}\) are divided into many levels because

FIG. 10. (a) Comparing eigen energies of the Woods–Saxon model and orbital levels of Al\(_{13}^-\) (ICOSAHEDRON), B\(_{13}^-\) (ICOSAHEDRON), Al\(_{12}\)H\(_{22}\)\(^2-\) (CAGE), and B\(_{12}\)H\(_{22}\)\(^2-\) (CAGE) at their most stable size. They are normalized so that the 1s and 2p orbitals become the same levels. The red line refers to the interchanging order. The number under the orbital shows the total number of electrons occupying from the lowest orbital to this orbital. Gray refers to an unoccupied orbital. (b) Comparing eigen energies of the Woods–Saxon model and orbital levels of Si\(_{10}\) and Si\(_{10}\)H\(_{16}\) at their most stable size. They are normalized so that the 1s and 2p orbitals become the same levels. The red line refers to the interchanging order. The number under the orbital shows the total number of electrons occupying from the lowest orbital to this orbital. Gray refers to an unoccupied orbital.
Si$_{10}$ has lower symmetry, but the order of the orbital group is not interchanged. These results are consistent with the fact that Al$_{13}^-$ (ICOSAHEDRON) and the Si$_{10}$ clusters have a metallic bond.

The other clusters did not follow the Woods–Saxon model. As for B$_{13}^-$ (ICOSAHEDRON), the 1fa energy is higher than 2p and the levels are interchanged. This resulted from this cluster being an unstable cluster. Al$_{12}$H$_2^2-$ (CAGE), B$_{12}$H$_2^2-$ (CAGE), and Si$_{10}$H$_{16}$ do not follow the Woods–Saxon model because they have a covalent bond. As for Al$_{12}$H$_2^2-$ (CAGE), the 1fa level is lower than 2s and 1fb is higher than 1ga. As for B$_{12}$H$_2^2-$ (CAGE), 1fb is higher than 1ga. 1d and 1f of Si$_{10}$H$_{16}$ resolve into 2 and 3 levels because of low symmetry. Then 1d, 1f, and 1g are interchanged complicatedly. The model cannot be used to compare with the B$_{13}^-$ (PLANE) and Al$_{13}^-$ (PLANE) orbital energies because they are far from spherical.

As a result, only Al$_{13}^-$ (ICOSAHEDRON) and Si$_{10}$ followed the Woods–Saxon model because these clusters have a metallic bond. Orbital shape and degeneracy depended on the symmetry of the clusters, and the order of the orbital level reflects the bonding nature of the clusters.

The potential, $V(r)$ of the Woods–Saxon model, is given as Eq. (1). To find parameters suitable for orbitals of the Al$_{13}^-$ and Si$_{10}$ metallic bonded clusters, we solved the Schrödinger equation in the radial direction using the difference method.

By considering metallic bonded clusters as having spherical symmetry, their potential can be approximated by the Woods–Saxon potential. Schrödinger’s equation can be solved numerically by transforming it into a difference equation, which is a kind of diagonalization problem. We made a computer program to find the
eigenvalues at any $V(r)$ parameters. We determined the most suitable parameters $V, R,$ and $a$ by comparing the solutions $E_{\text{calc}}$ and Gaussian results $E_{\text{Gaussian}}$ for each cluster.

The solving procedure for the Al$_{13}^-$ and Si$_{10}$ clusters was composed of three steps. (1) Coordinate the 1s and 2p eigenvalues to that of the result of Gaussian by fitting $V.$ (2) Calculate the root mean square of the difference of each orbital energy ($\Sigma (E_{\text{Gaussian}} - E_{\text{calc}})^2$). A lower root mean square will result in more suitable parameters. (3) Perform the same calculation by changing $R$ and $a,$ and determine the most suitable parameters $V, R,$ and $a$ [Fig. 11(a)]. We show the shapes of $V(r)$ [Fig. 11(b)] and the orbital energy [Fig. 11(c)]. The results $a > R$ for Al$_{13}^-$ and Si$_{10}$ clusters are different from $a < R,$ which is the result for the typical metallic bonding Na cluster. The shape of the potential approaches the square-well when $a < R$ and the harmonic oscillator when $a > R.$ Therefore, the above difference means that the bonding nature of the Na cluster is more metallic than those of Al$_{13}^-$ and Si$_{10}$ clusters.

On the other hand, the interchanges of energy levels as shown in unstable or covalent bonding clusters in Fig. 10 have not occurred by changing the parameters $V, R,$ or $a.$

The most suitable $R$ of Al$_{13}^-$ in the Woods–Saxon model was 1.35 times the radius of the Al$_{13}^-$ cluster, which is the distance between the center and the outer atom of the cluster, and $R$ of Si$_{10}$ in the Woods–Saxon model was 1.54 times the radius of the Si$_{10}$ cluster. These results are reasonable, when the atomic radii are considered.

VI. CONCLUSION

The HOMO of a stable cluster is bonding, and the HOMO of an unstable cluster is antibonding. The overall features of cluster size dependences of the orbital energy for B$_{13}^-$ (ICOSAHEDRON) and Al$_{13}^-$ (ICOSAHEDRON) are almost the same, when the size and the energy are normalized. The normalized factors for size and energy are near the ratio of the radii of the atomic outer s orbitals and the ratio of the s orbital energies, respectively. On the other hand, the difference of the most stable cluster size of B$_{13}^-$ (ICOSAHEDRON) and Al$_{13}^-$ (ICOSAHEDRON) depends on the ratio of the atomic outer p orbitals. The 2p orbital of B does not have an inner p orbital, and the size is almost the same as the 2s orbital; however, the 3p orbital of Al has an inner 2p orbital and the size is larger than that of the 3s orbital. From these facts, the HOMOs of B$_{13}^-$ (ICOSAHEDRON) and Al$_{13}^-$ (ICOSAHEDRON) with the most stable size are antibonding and unstable, and bonding and stable, respectively. When the order of the orbital energies of the cluster follows the Woods–Saxon model, the bonding nature of the cluster is metallic and a covalent bonded cluster will not follow this model. The Woods–Saxon model for Al$_{13}^-$ (ICOSAHEDRON) and Si$_{10}$ with the optimized parameters provides reasonable orbital energies and potential shapes. Therefore, we propose the way to judge whether a cluster with spherical symmetry has a metallic bond or not by investigating whether the orbital energies of the cluster follow those obtained by the Woods–Saxon model.

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