Consideration of Superatomic Hybrid Orbital in superatom M@Al_{12} (M = Be, Mg, Ca, Sr)

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Abstract. We introduce a superatom, which is regarded as a modern alchemy and has been studied around the world. The superatom is a nanocluster composed of multiple atoms, for example Al_{13}. Very interestingly, the “superatom” can mimic the chemical properties of “atom”, for example, the superatom Al_{13} exhibits the character of halogen atom, such as Cl. If this superatom is synthesized to an appropriate size freely, there is the possibility to be placed as an "artificial atom" in a three-dimensional periodic table, such as the conventional two-dimensional periodic table. In recent years, the exhaustion of rare metals has become a big problem, so that in the next generation of materials and devices, the superatom play as an important role, and it is expected to be used for various materials or as a substitute for expensive metal catalysts such as Pt. From these points of view, the superatom have been studied all over the world up to now, but there is not much studies on their electronic structures. Therefore, in this study, we have analyzed the electronic states of the chalcogen-encapsulated type superatom M@Al_{12} (M = Be, Mg, Ca, Sr) by means of DV-Xα molecular orbital calculation. Our research revealed that the electronic configuration of the superatom, which changed only the central atom, depends largely on the kind of doped atom. And we can also confirm the “superatomic hybrid orbitals (SAHOs)” composed of superatomic orbitals (SAOs), and chalcogen characteristics.

1. Introduction
A nanocluster composed of fewer metal atoms and stably present, and having chemical properties like atoms is called a superatom. If these can be freely synthesis, it can be arranged as a three-dimensional periodic table, such as the conventional two-dimensional periodic table. A superatom that is structured to an appropriate size and synthesized to mimic the atomic chemistry can be considered an "artificial element". If we can perform such as the "modern alchemy" that produces the superatom having the same chemical character of an expensive metals from cheaper metals, we may be able to explore the new era of materials science.

The most famous example of the superatom is Al_{13} having an icosahedral structure (I_h), and it is well known that has the chemical properties similar to a halogen atom such as Cl atom. The main reason for having the same chemical property is explained by both “atomic orbital” and “electron configuration”. In the case of an atom, it has atomic orbitals and electron configurations can be determined such as 1s^2, 2s^2, 2p^6, … (written by small letter). In contrast, superatom have orbitals and the special configurations called “superatomic orbitals(SAOs)” according to the jellium model, such as 1S^2, 1P^6, 1D^{10}, 2S^2, 1F^{14}, … (written by capital letter).
For example, the III-group atoms like Al have 3 electrons as a valence electrons. They are all trivalent atoms and their 13 atom cluster have, totally, 39 valence electrons. The electronic configurations of the superatom Al\textsubscript{13} and Cl atom are exhibited in Fig. 1. In the figure, both the superatom Al\textsubscript{13} and Cl atom have five electrons each in the outermost shells 2P and 3p orbitals. This indicates that obtaining a single electron results in a stable structure as a closed shell structure 2P\textsuperscript{6} or 3p\textsuperscript{6}, respectively. Mainly from these points, the superatom is considered to have the chemical properties of the halogen atom Cl.

2. Computational details

We determined the coordinates of the calculation cluster models from the experimental results of a bond lengths and the molecular structures from past papers, and calculated the electronic state calculations by means of the DV-X\alpha molecular orbital method. Then, we confirmed the spatial extent of the wave functions using the application “VESTA”. The calculated cluster models M@Al\textsubscript{12} (M = Be, Mg, Ca, Sr) used for the calculation is shown in Fig. 2. The molecular structural data of the most famous superatom Al\textsubscript{13} has been employed. So this models have an icosahedral structure in which the distance between Al-Al is 2.80 Å, whereas the distance between M-Al is 2.66 Å, respectively. In this study, we replace only the central metal of this calculation model with M and compare the electronic states among them.

![Fig. 2. Model of M@Al\textsubscript{12} (M = Be, Mg, Ca, Sr).](image)

3. Result and discussion

First, the result of the energy levels of Be@Al\textsubscript{12} obtained by an electronic state calculation are shown in Figs. 3 and 4 (Fig. 4 is partially enlarged of Fig. 3). In these figures, the horizontal and vertical axes are the number of molecular orbitals and, the energy levels, respectively. From the result of Fig. 4, it is revealed that the typical energy level dispersion expected in the case of the superatom can be confirmed after around molecular orbital number #62. These molecular orbitals after #60 can be assigned the SAOs composed of valence electrons from Al and Be.
Then, we confirm the 3D spatial distribution of the wave functions of SAOs using VESTA. As a result of substituting with Be into Al\textsubscript{13}, the SAOs and the electron configuration can be assigned as 1S\textsuperscript{2}, 1P\textsuperscript{6}, 1D\textsuperscript{10}, 2S\textsuperscript{2}, 1F\textsuperscript{14}, 2P\textsuperscript{4} which completely follows the jellium model. Similarly, results of substituting the central metal of Mg, Ca, and Sr into Al\textsubscript{13} are summarized in Fig. 5.

In the case of Mg substituting, the electron configuration is assigned as 1S\textsuperscript{2}, 1P\textsuperscript{6}, 1D\textsuperscript{10}, 2S\textsuperscript{2}, 1F\textsuperscript{14}, 2P\textsuperscript{4} follow the jellium model as well as the previous result of Be substituting. Next, in the case of Ca substituting, we could confirm a significant phenomenon of the energy level structure, in which eight 1F orbitals appeared instead of 2S orbital. The images of the energy level and SAOs of Ca@Al\textsubscript{12} are shown in Fig. 6.
For explaining the origin of these SAOs, Fig. 7 shows the Mulliken population analysis which show the component of each SAO. Generally, in the case of 2S, the 4s orbital of the Ca atom is expected to be appeared, whereas in this result the 4s orbitals has been dispersed into the molecular orbital number 83, 84, 85 and 86. From this result, the eight 1F orbitals can be realized as a result of the hybridized orbital between the 2S and 1F orbitals. Therefore, the SAOs consists of 1F and 2S of the Ca@Al\(_{12}\) are named as SF superatomic hybrid orbitals (SAHOs), and the electron configuration is assigned as 1S\(^2\), 1P\(^6\), 1D\(^{10}\), SF\(^{16}\), 2P\(^4\) in the result of Ca@Al\(_{12}\). Finally, in the case of doping Sr, the order of 2S and 1F were switched. However, as well as in the case of doping Be and Mg, seven 1F and one 2S SAOs could be confirmed, and the electron configuration was assigned as 1S\(^2\), 1P\(^6\), 1D\(^{10}\), 1F\(^{14}\), 2S\(^2\), 2P\(^4\). Comparing the energy levels in Fig. 7, it can be revealed that the energy gap between 2S and 1F SAOs decreases as the atomic number of the central atom increase. When Be or Mg is doped, the 2S orbital has lower energy than that of 1F orbitals. But in case of Sr is substituted, the 2S orbital is higher than that of 1F orbitals. This is considered to be affected by the size of the s orbital between small s orbital such as Be and Mg atoms and large s orbital such as Sr atom. Therefore, when Ca with medium size is substituted, the energy of 1F and 2S orbitals are considered to form a
hybridized orbitals (that is SF SAHO). In addition, all electron configurations of M@Al\textsubscript{12} calculated in this work are occupied up to the 2P\textsuperscript{4}, and it is possible to achieve a closed shell structure by acquiring two more electrons. This indicates that these M@Al\textsubscript{12} superatoms have the possibility of ability to mimic the chalcogen atoms.

4. Conclusion
We clarified the electronic states such as superatomic orbitals and electronic configurations for M@Al\textsubscript{12} (M = Be, Mg, Ca, Sr) which changed only the central metal. We confirmed the SAOs according to the jellium model, especially in the cases of the Be and Mg substituted M@Al\textsubscript{12}. However, when Ca was substituted, the significant SF hybridized orbitals consisting of 2S and 1F orbitals were confirmed. And it was also found that novel these superatoms could be a mimic of chalcogen atoms due to the relationship of electron configuration. In the future, it is necessary to discuss the SAHO in other various superatoms.

References
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