

## ARTICLE

## Stable High-Energy Density Super-Atom Clusters of Aluminum Hydride

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With the concept of super-atom, first principles calculations propose a new type of super stable cage clusters  $\text{Al}_n\text{H}_{3n}$  that are much more energetic stable than the well established clusters,  $\text{Al}_n\text{H}_{n+2}$ . In the new clusters, the aluminum core-frame acts as a super-atom with  $n$  vertexes and  $2n$  Al–Al edges, which allow to adsorb  $n$  hydrogen atoms at the top-site and  $2n$  at the bridge-site. Using  $\text{Al}_{12}\text{H}_{36}$  as the basic unit, stable chain structures,  $(\text{Al}_{12}\text{H}_{36})_m$ , have been constructed following the same connection mechanism as for  $(\text{AlH}_3)_n$  linear polymeric structures. Apart from high hydrogen percentage per molecule, calculations have shown that these new clusters possess large heat of formation values and their combustion heat is about 4.8 times of the methane, making them a promising high energy density material.

**Key words:** High-energy density, Super-atom, First principles, Cluster of aluminum hydride

## I. INTRODUCTION

Aluminum and aluminoborane clusters with high hydrogen capacity and attractive hydrogen desorption temperature are considered to be good candidates for hydrogen storage [1]. Aluminum clusters can also be used as catalysis and propulsion material [2, 3]. The central focus on many theoretical and experimental studies is to find new stable clusters, to understand the formation mechanism and to discover their unique properties. For aluminum hydride clusters of rich Al phase ( $1 \leq m \ll n$  in  $\text{Al}_n\text{H}_m$ ), the free electron is dominant in the system and the stability can be well explained by the jellium model [4, 5]. With more H atoms adsorbed on the aluminum substrate, electrons in the hydrogenated system are believed to be more localized. However, the mechanism for the stability of rich H phase ( $n < m$  in  $\text{Al}_n\text{H}_m$ ) is still largely unknown. The most exciting findings so far is probably the experimental observation of an unexpected stable specie,  $\text{Al}_4\text{H}_6$  [3], which was found to obey the so-called Wade-Mingos rules [6–8]. Following this rule, it was confirmed that in general  $\text{Al}_n\text{H}_{n+2}$  clusters should be stable [9, 10]. However, one can notice that in each  $\text{Al}_n\text{H}_{n+2}$  cluster, there are still  $(2n - 2)$  free electrons left, which can in principle be saturated by extra hydrogen atoms if we consider the Al cluster as a super-atom.

In this work, we show new stable clusters for alu-

minum hydrides that fulfill the super-atom principle. The structures of two stable cage aluminum hydride  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$  have been analyzed in detail. We have also shown that the cage  $\text{Al}_{12}\text{H}_{36}$  cluster can be used as a basic unit to form  $(\text{Al}_{12}\text{H}_{36})_m$  chain structure with the same bonding mechanism as that of  $(\text{AlH}_3)_n$  polymers. The combustion heat of new clusters has also been estimated and its potential usage as the energy material is discussed.

## II. COMPUTATION DETAILS

Structure optimization and electronic structure calculations were performed using Perdew-Wang exchange and gradient-corrected correlation functional (PW91) [11] with 6-311G(d,p) Gaussian basis set as implemented in Gaussian 03 package [12]. The PW91 functional is known to give good description for the geometry and electronic structure of aluminum hydrides [9, 13]. The Geometry optimization has been done without symmetry constraint. Moreover, analytic Hessian matrix has also been calculated to guarantee that the obtained final structures are true minimum.

## III. RESULTS AND DISCUSSION

A. Stable structures of  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$ 

After considering many different structural arrangements, we finally find the core structure of the  $\text{Al}_n$  cluster that is capable of adsorbing  $3n$  hydrogen atoms. Two best examples are  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$  as shown in

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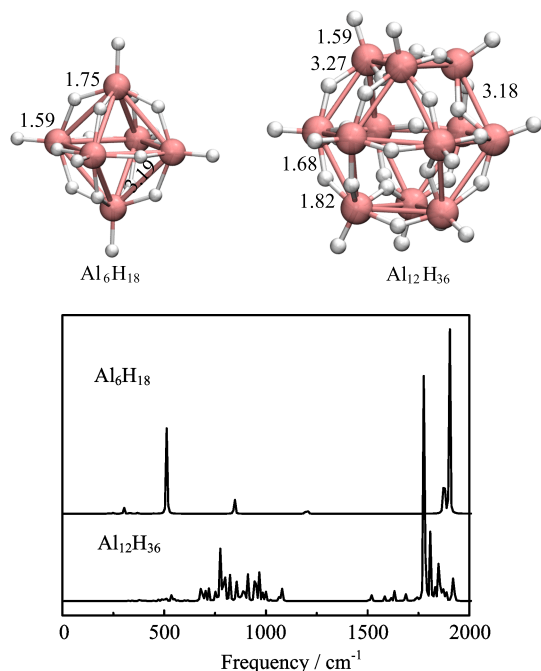


FIG. 1 The optimized structures of  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$ , and the corresponding infrared spectra.

Fig.1. In these structures, one can see  $n$  top-site hydrogen atoms and  $2n$  bridge hydrogen atoms. For  $\text{Al}_6\text{H}_{18}$ , the optimized geometry is of octahedral symmetry. The Al–Al bond length among  $\text{Al}_6\text{H}_{18}$  is 3.19 Å, much longer than that in pure aluminum clusters, demonstrating that the direct interaction between Al atoms is greatly weakened due to the absorption of abundant hydrogen atoms. Actually, with hydrogen atoms adsorbed on bridge sites, the original Al–Al linkage is replaced by three centers Al–H–Al bridge bond, as what was found in  $\text{Al}_4\text{H}_6$  [3]. The terminal Al–H bond length is 1.59 Å, which is a typical covalence bond length between Al and H atoms. The bond length between bridge H and Al atoms among  $\text{Al}_6\text{H}_{18}$  is 1.75 Å. Its infrared spectrum shows two main peaks at around 900 and 1800  $\text{cm}^{-1}$ , resulting from the motion of hydrogen atoms in the system. For  $\text{Al}_{12}\text{H}_{36}$ , the most stable cage structure has a  $C_2$  symmetry, as shown in Fig.1. Although an octahedral symmetric configuration with 12 terminal and 24 bridge H atoms was constructed as an initial configuration, the geometry relaxation has led to the reduced symmetry. The predicted infrared spectrum for this stable  $\text{Al}_{12}\text{H}_{36}$  cluster is broadened because of its low symmetry, compared with  $\text{Al}_6\text{H}_{18}$ . The average Al–Al bond length among  $\text{Al}_{12}\text{H}_{36}$  is 3.47 Å, which is longer than that in  $\text{Al}_6\text{H}_{18}$ , inferring that with the cluster size increasing, the interaction between two adjacent aluminum atoms gets even weaker. The average bond length between bridge H and Al atoms among  $\text{Al}_{12}\text{H}_{36}$  is about 1.76 Å and the terminal Al–H bond length remains 1.59 Å. From these geometry param-

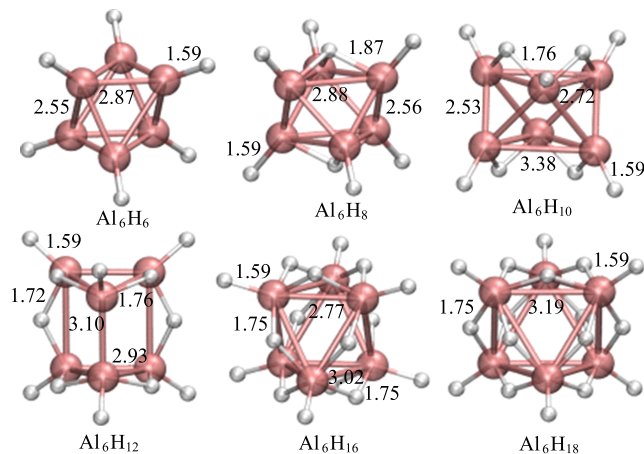


FIG. 2 The optimized structures of  $\text{Al}_6\text{H}_6$ ,  $\text{Al}_6\text{H}_8$ ,  $\text{Al}_6\text{H}_{10}$ ,  $\text{Al}_6\text{H}_{12}$ ,  $\text{Al}_6\text{H}_{16}$ , and  $\text{Al}_6\text{H}_{18}$ .

ters, one can conclude that these two cage clusters have the same structure characteristics.

## B. $\text{Al}_6\text{H}_m$ and $\text{Al}_{12}\text{H}_m$ series

The discovery of the stable  $\text{Al}_4\text{H}_6$  cluster has attracted considerable attention [3]. Such an unexpected cluster was found to follow the so-called Wade-Mingos rule [6]. For rich H phase, the Wade-Mingos clusters,  $\text{Al}_n\text{H}_{n+2}$ , have become the most important species in the whole aluminum hydride family [9]. It is worth noting that the  $\text{Al}_6\text{H}_{18}$  super-atom cluster possesses the same octahedral Al skeleton as that of Wade-Mingos cluster,  $\text{Al}_6\text{H}_8$ , whereas the Al frames for  $\text{Al}_{12}\text{H}_{36}$  and  $\text{Al}_{12}\text{H}_{14}$  are different. The Wade-Mingos cluster  $\text{Al}_{12}\text{H}_{14}$  has an icosahedral Al frame, while it is an octahedral frame for super-atom cluster  $\text{Al}_{12}\text{H}_{36}$ . In order to understand the formation of the new super-atom clusters, we have examined the structural evolution of the  $\text{Al}_6\text{H}_m$  and  $\text{Al}_{12}\text{H}_m$  series. With the geometry optimization, for the  $\text{Al}_6\text{H}_m$  series, stable structures with  $m=6, 8, 10, 12, 16$ , and 18, have been obtained, while for the  $\text{Al}_{12}\text{H}_m$ , structures of  $m=12, 14, 16, 20$ , and 36, are identified.

We start with  $\text{Al}_6\text{H}_6$  cluster for the  $\text{Al}_6\text{H}_m$  series as shown in Fig.2. It is found that the optimized  $\text{Al}_6\text{H}_6$  is of  $D_{3d}$  symmetry and each hydrogen atom interacts with aluminum substrate through covalence bond on each top site. The two added hydrogen atoms in  $\text{Al}_6\text{H}_8$  occupy the hollow sites in two opposite faces and the system of the whole cluster remains the same as that of  $\text{Al}_6\text{H}_6$ . For  $\text{Al}_6\text{H}_{10}$  cluster, the added four new hydrogen atoms prefer to the bridge sites and the Al core-structure is slightly distorted, resulting in a  $C_{2h}$  symmetry. With two more H atoms supplied, the Al skeleton of the  $\text{Al}_6\text{H}_{12}$  cluster undergoes a noticeable change. The triangle connection of the Al atoms turns into the quadrilateral and the total symmetry of the  $\text{Al}_6\text{H}_{12}$  be-

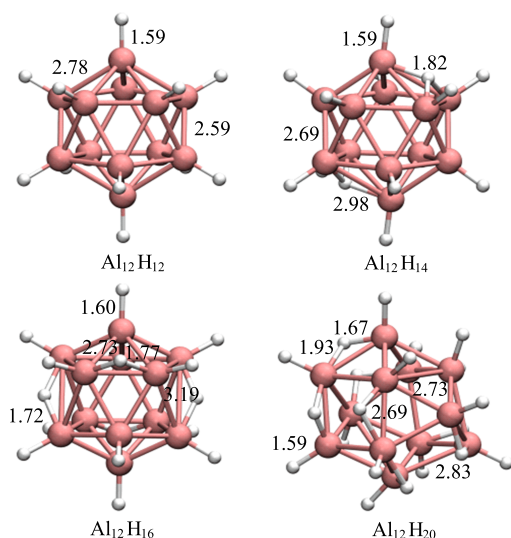


FIG. 3 The optimized structures of  $\text{Al}_{12}\text{H}_{12}$ ,  $\text{Al}_{12}\text{H}_{14}$ ,  $\text{Al}_{12}\text{H}_{16}$ , and  $\text{Al}_{12}\text{H}_{20}$ .

comes  $\text{C}_{2v}$ . With many attempts, we failed to find stable 3D structure for  $\text{Al}_6\text{H}_{14}$ , for which the aluminum core-frame is dissolved after a long time optimization. For  $\text{Al}_6\text{H}_{16}$ , the Al skeleton returns back to its original appearance as in  $\text{Al}_6\text{H}_6$ . The extra hydrogen atoms are all adsorbed at the bridge sites. The geometry of super-atom cluster  $\text{Al}_6\text{H}_{18}$  resembles well the structure of the cluster  $\text{Al}_6\text{H}_{16}$  with  $\text{D}_{2h}$  symmetry.

The related structures of  $\text{Al}_{12}\text{H}_m$  clusters are collected in Fig.3. Our optimized  $\text{Al}_{12}\text{H}_{12}$  cluster possesses a  $\text{D}_{5d}$  symmetry, in close agreement with the earlier reported structure of  $\text{I}_h$  symmetry [14]. In this case, each hydrogen atom is bonded to an aluminum atom on the top site. The two extra hydrogen atoms in the optimized  $\text{Al}_{12}\text{H}_{14}$  of  $\text{D}_{3d}$  symmetry occupy two opposite hollow sites, similar to the case of  $\text{Al}_6\text{H}_8$ . However, for  $\text{Al}_{12}\text{H}_{16}$  cluster all four extra hydrogen atoms prefer to the bridge sites with approximately icosahedral skeleton. When four more hydrogen atoms are added to form  $\text{Al}_{12}\text{H}_{20}$ , the symmetry of  $\text{Al}_{12}$  core-frame is gradually changed from semi-icosahedral to semi-octahedral to provide suitable edges for adsorbing hydrogen atoms. We have found that further adding hydrogen atoms between 20 and 36, the cluster does not lead to any stable structures and the aluminum skeleton is always broken down. The  $\text{Al}_{12}\text{H}_{36}$  is a stable structure with octahedral aluminum core-frame. In general, for  $\text{Al}_{12}$  cluster, the octahedral core-frame tends to adsorb more hydrogen atoms than the icosahedral one. It is also important to note that not all  $\text{Al}_n\text{H}_m$  cluster has a stable configuration. There are certain magic numbers involved.

There are several important parameters that are useful for judging the stability of a cluster, namely the energy gap ( $E_g$ ), the vertical electron affinity (VEA) and the vertical ionization potential (VIP). Normally, a cluster with larger  $E_g$ , lower VEA and higher VIP is

TABLE I Calculated HOMO-LUMO energy gap ( $E_g$ ), BE, VEA, and VIP for different  $\text{Al}_6\text{H}_m$  and  $\text{Al}_{12}\text{H}_m$  clusters. All values are in eV.

	$E_g$	BE	VEA	VIP
$\text{Al}_6\text{H}_6$	0.54	2.33	2.86	7.43
$\text{Al}_6\text{H}_8$	2.83	2.43	0.73	7.51
$\text{Al}_6\text{H}_{10}$	2.08	2.39	1.50	7.62
$\text{Al}_6\text{H}_{12}$	3.23	2.47	0.79	7.97
$\text{Al}_6\text{H}_{16}$	1.44	2.39	2.12	7.62
$\text{Al}_6\text{H}_{18}$	3.28	2.44	1.85	9.14
$\text{Al}_{12}\text{H}_{12}$	0.23	2.52	4.21	7.91
$\text{Al}_{12}\text{H}_{14}$	2.50	2.56	1.91	7.84
$\text{Al}_{12}\text{H}_{16}$	2.34	2.50	2.05	7.75
$\text{Al}_{12}\text{H}_{20}$	1.77	2.43	2.85	7.93
$\text{Al}_{12}\text{H}_{36}$	4.08	2.46	1.41	9.00

often more stable. The calculated values for  $\text{Al}_6\text{H}_m$  and  $\text{Al}_{12}\text{H}_m$  series are summarized in Table I. The Wade-Mingos clusters  $\text{Al}_6\text{H}_8$  and  $\text{Al}_{12}\text{H}_{14}$  are known to be very stable, which are clearly demonstrated by their energetic properties. By using  $\text{Al}_6\text{H}_8$  as the reference one, we can immediately see that  $\text{Al}_6\text{H}_6$ ,  $\text{Al}_6\text{H}_{10}$  and  $\text{Al}_6\text{H}_{16}$  are less stable species, while  $\text{Al}_6\text{H}_{12}$  and  $\text{Al}_6\text{H}_{18}$  are comparably stable, if not more stable. For the  $\text{Al}_{12}\text{H}_m$  series, it can be found that the Wade-Mingos cluster  $\text{Al}_{12}\text{H}_{14}$  is much more stable than  $\text{Al}_{12}\text{H}_{12}$  and  $\text{Al}_{12}\text{H}_{20}$ , slightly more stable than  $\text{Al}_{12}\text{H}_{16}$ . However, it is definitely much less stable than  $\text{Al}_{12}\text{H}_{36}$ . In general, both super-atom clusters,  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$ , possess very good energetic properties that guarantees the stability. It is worth noting that the large gap energies of 3.28 and 4.06 eV for super-atom clusters  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$  are comparative with that of  $(\text{AlH}_3)_n$  polymer. Based on all these results, one can at least conclude that it is possible to find more stable hydrogen rich aluminum hydrides than what the Wade-Mingos rule allows.

### C. Chemical bond between the hydrogen and the aluminum atoms

We have used different ways to illustrate the chemical bond between the hydrogen and the aluminum atoms. The first one is the deformation of electron density (ED), which is obtained by a simple relation,  $\text{ED}_{\text{Al}_n\text{H}_{3n}} - \text{ED}_{\text{Al}_n\text{H}_n} - \text{ED}_{2n\text{H}}$ , *i.e.* subtracting electron density of  $\text{Al}_n\text{H}_n$  (only terminal Al-H bonds involved) and those individual bridge hydrogen atoms from the total electron density of  $\text{Al}_n\text{H}_{3n}$ . With it, one can determine how these bridge hydrogen atoms are involved in its chemical bonding with the aluminum substrate, and verify whether the valence bond between top site hydrogen atoms and aluminum atoms are affected by bridge hydrogen atoms.

In Fig.4, we present both depletion and excess of elec-

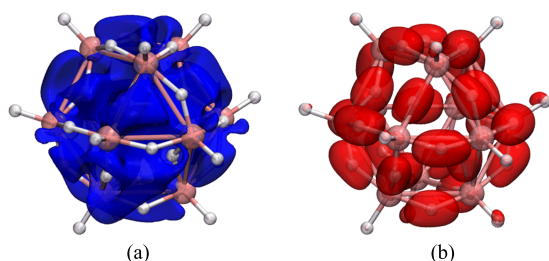


FIG. 4 (a) The depletion and (b) excess of electron density with the bridged H atoms adsorbed on  $\text{Al}_{12}\text{H}_{36}$ .

tron density for  $\text{Al}_{12}\text{H}_{36}$  as a result of adsorbed bridge H atoms. We can see that there is no obvious electron deformation between the terminal Al–H bonds. The electron density around the hollow site of the aluminum substrate decreases, but it increases around the H atoms on the bridges. That is to say, the added H atoms on bridges do not affect the covalent bond between the terminal Al and H but completely mix with Al atoms through the covalent bonding and contribute to the formation of three centers Al–H–Al. Accompanying with  $2n$  bridged hydrogen atoms, all free electrons in aluminum clusters are totally localized around three centers Al–H–Al bridge bonds.

We have also plotted out in Fig.5 the orbital distributions of  $\text{Al}_{12}\text{H}_{12}$ ,  $\text{Al}_{12}\text{H}_{14}$ , and  $\text{Al}_{12}\text{H}_{36}$  to further examine the nature of the chemical bonds in these clusters. In Fig.5 each orbital is partitioned into three parts that are contributed from the aluminum core-frame, top-site hydrogen atoms and bridge/hollow-site hydrogen atoms, respectively. It can be seen that the energy positions of hydrogen-induced orbitals are highly dependent on the adsorption sites of hydrogen atoms. The orbitals involved of terminal Al–H bonds are confined to the energy region from  $-11$  to  $-7$  eV in all these clusters, while the contribution of bridge hydrogen atoms spread over the whole energy spectrum, well mixed with those orbitals of Al atoms. This is particularly obvious in  $\text{Al}_{12}\text{H}_{36}$  cluster, indicating that these two types of hydrogen atoms interact with the aluminum substrate differently. The hydrogen atoms on the top site form covalence bonds with aluminum atoms and these covalence bonds are not affected by the presence of bridged hydrogen atoms. The bridged hydrogen atoms contribute their electrons to the whole system. In  $\text{Al}_{12}\text{H}_{36}$ , the contributions of hydrogen atoms in all orbitals are almost equal to those of aluminum atoms.

It can be seen from the energy level distribution of  $\text{Al}_{12}\text{H}_{12}$  in Fig.5, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is very small, but the gap between LUMO and (LUMO+1) gap quite large. This indicates that the  $\text{Al}_{12}\text{H}_{12}$  is not stable in general. To add two hydrogen atoms, the LUMO of  $\text{Al}_{12}\text{H}_{12}$  is filled up and the resulting  $\text{Al}_{12}\text{H}_{14}$  cluster become very stable. This picture is consistent with the pro-

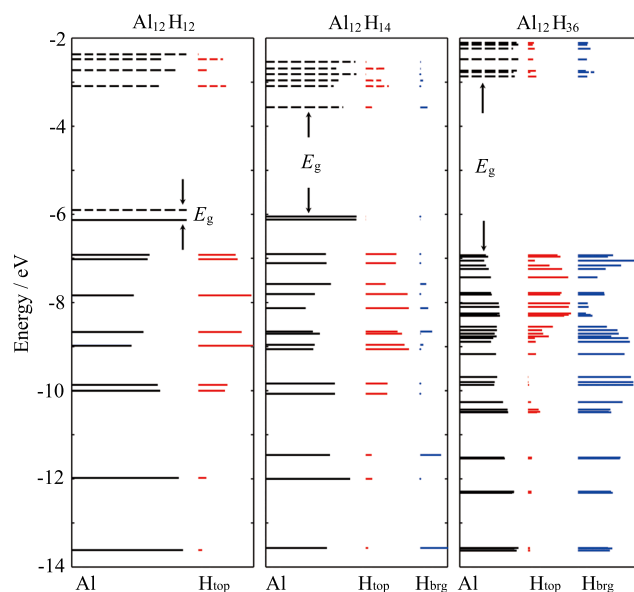


FIG. 5 The energy level distribution with partitioned contributions from the aluminum substrate (Al), top-site hydrogen atoms ( $\text{H}_{\text{top}}$ ) and bridge/hollow-site hydrogen atoms ( $\text{H}_{\text{brg}}$ ) for  $\text{Al}_{12}\text{H}_{12}$ ,  $\text{Al}_{12}\text{H}_{14}$ , and  $\text{Al}_{12}\text{H}_{36}$ , respectively.

posed Wade-Mingos rules for  $\text{Al}_4\text{H}_6$  [3]. Wade-Mingos rules, also known as polyhedral skeletal electron pair approach, are empirical theory based on bonding models. With accurate molecular orbital calculation, we can now provide a clear molecular orbital view on the stability of  $\text{Al}_{12}\text{H}_{14}$ .

With the concept of super-atom, we can also relate the stability of a cluster to its special shell structure of electronic distribution. In Fig.6, we have plotted out the orbital pictures of all valence orbitals for  $\text{Al}_{12}\text{H}_{12}$  and  $\text{Al}_{12}\text{H}_{14}$  and calibrated them with corresponding atomic orbitals. It can be seen that the ground state electronic structure of  $\text{Al}_{12}\text{H}_{12}$  can be presented by a super-atom with a configuration of  $1s^2 1p^6 1d^{10} 1f^6 2s^2 2p^6 2d^{10} 1f^6$ . It is known that the filled f shell should hold 14 electrons, while there exist only 12 f electrons in  $\text{Al}_{12}\text{H}_{12}$ . Moreover, the LUMO of  $\text{Al}_{12}\text{H}_{12}$  is also f orbital and LUMO+1 is of s character. The small HOMO-LUMO gap and large LUMO-LUMO+1 gap could be understood from the fact that they fall into either the same or different shells. When two hydrogen atoms are added, the symmetry of the system is reduced from  $D_{5d}$  to  $D_{3d}$ , resulting in the energy adjustment for related molecular orbital. The ground state electronic structure of  $\text{Al}_{12}\text{H}_{14}$  has a configuration of  $1s^2 1p^6 1d^{10} 1f^6 2s^2 2p^2 2d^2 2p^4 1f^2 2d^8 1f^6$ , consisting of fully occupied two s shells, two p shell, one d shell and one f shell. We can say that the extremely stability of  $\text{Al}_{12}\text{H}_{14}$  comes from its closed shell-like electronic distribution.

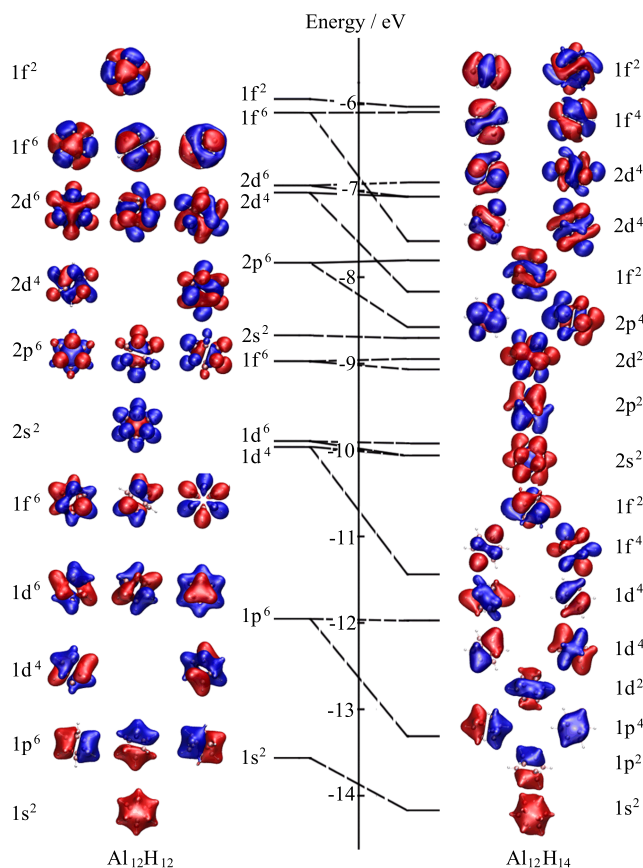


FIG. 6 The molecular orbital pictures of valence orbitals for  $\text{Al}_{12}\text{H}_{12}$  and  $\text{Al}_{12}\text{H}_{14}$ .

#### D. Thermodynamic properties of $\text{Al}_6\text{H}_8$ and $\text{Al}_{12}\text{H}_{36}$

One important thermodynamic property of a molecule is the heat of formation. We have used atomization reaction method to calculate it. In this approach, the  $\text{Al}_n\text{H}_m$  is decomposed into Al and H atoms, and the heat of formation for  $\text{Al}_n\text{H}_m$  is calculated with the help of the reaction:  $\text{Al}_n\text{H}_m \rightarrow n\text{Al} + m\text{H}$ . We firstly calculate the heat of formation for molecular  $\text{Al}_n\text{H}_m$  at 0 K ( $\Delta_f H_M^\ominus(0\text{ K})$ ), following the relationship:

$$\Delta_f H_M^\ominus(0\text{ K}) = \sum x \Delta_f H_X^\ominus(0\text{ K}) - D_0(\text{M}) \quad (1)$$

here,  $\Delta_f H_X^\ominus(0\text{ K})$  stands for the heat of formations for constituent atomic elements (X) at 0 K which are taken from the reference [15];  $D_{0,\text{Al}_n\text{H}_m}$  stands for the atomization energy which is calculated by the corresponding energy difference from the inclusion of zero-point vibration energy correction, *i.e.*,

$$D_{0,\text{Al}_n\text{H}_m} = (nE_{0,\text{Al}} + mE_{0,\text{H}}) - (E_{0,\text{Al}_n\text{H}_m} + E_{\text{ZPE},\text{Al}_n\text{H}_m}) \quad (2)$$

We introduce temperature correction represented as  $H_{\text{Al}_n\text{H}_m}^\ominus(298\text{ K}) - H_{\text{Al}_n\text{H}_m}^\ominus(0\text{ K})$  and  $\sum x[H_X^\ominus(298\text{ K}) - H_X^\ominus(0\text{ K})]$

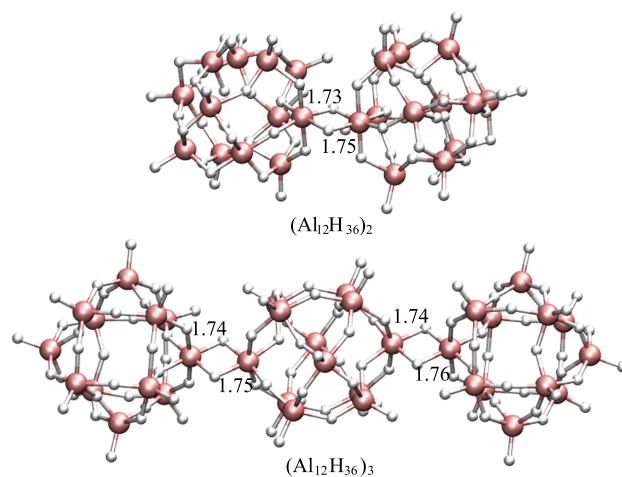


FIG. 7 Optimized chain structures of  $(\text{Al}_{12}\text{H}_{36})_2$  and  $(\text{Al}_{12}\text{H}_{36})_3$ .

$H_X^\ominus(0\text{ K})$ ], here, the first part is the enthalpy correction for the molecule, obtained from the frequency analysis; the latter part is the enthalpy corrections for the aluminum and hydrogen atoms, referring to the chemical database [16]. Finally, we get the the heat of formation for molecular  $\text{Al}_n\text{H}_m$  at 298 K from the relationship:

$$\Delta_f H^\ominus(298\text{ K}) = \Delta_f H_{\text{Al}_n\text{H}_m}^\ominus(0\text{ K}) + [H_{\text{Al}_n\text{H}_m}^\ominus(298\text{ K}) - H_{\text{Al}_n\text{H}_m}^\ominus(0\text{ K})] - \sum x[H_X^\ominus(298\text{ K}) - H_X^\ominus(0\text{ K})] \quad (3)$$

With all these values in hand, we have obtained the heat of formation for  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$  at 298 K, which is 0.55 and 1.00 MJ/mol, respectively. These are comparable high positive heat of formation values, indicating that these clusters can be potential high energy density material. We have also calculated their combustion heat to the products,  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}$ , which are found to be 4.90 and 5.74 MJ/mol for  $\text{Al}_6\text{H}_{18}$  and  $\text{Al}_{12}\text{H}_{36}$ , respectively. These values are about 4.8 times of the methane, and three times of high energy material  $\text{Al}_4\text{H}_6$  [3].

#### E. The formation of $(\text{Al}_{12}\text{H}_{36})_n$ chains

The crystal structures of aluminum trihydride possess several different polymorphs with covalent  $\text{AlH}_3$  cluster as the smallest structure unit. We have found that the super-atom clusters,  $\text{Al}_{6n}\text{H}_{18n}$ , can function the same way as  $\text{AlH}_3$  to form chain-like polymeric structures with retained structure characteristics. With the number of hydrogen atoms three times as many as aluminum atoms per molecule, materials made from  $\text{Al}_{6n}\text{H}_{18n}$  super-atom clusters can store up to 10.1% of hydrogen just like aluminum trihydride. The unique thermodynamic properties could make them promising high-energy high-density material (HEDM).

We have constructed different  $(\text{Al}_{12}\text{H}_{36})_n$  conformations with the  $\text{Al}_{12}\text{H}_{36}$  cluster as the basic constructive unit. In Fig.7, the optimized most stable structures for  $(\text{Al}_{12}\text{H}_{36})_2$  and  $(\text{Al}_{12}\text{H}_{36})_3$  are illustrated. In these oligomers, two top-site hydrogen atoms on two different  $\text{Al}_{12}\text{H}_{36}$  clusters have served as the connectors. The distance between the hydrogen and aluminum atoms of two clusters lies in 1.70–1.90 Å. It is important to note that for each  $\text{Al}_{12}\text{H}_{36}$  molecule, apart from one top hydrogen atom involved in the connection, the entire  $\text{Al}_{12}\text{H}_{36}$  cage structure remains its unique geometry characteristics. All twelve top hydrogen atoms in  $\text{Al}_{12}\text{H}_{36}$  cluster can have the possibility to connect to another cluster. It is thus highly feasible to form 3-dimensional interconnected  $\text{Al}_{12}\text{H}_{36}$  structures.

#### IV. CONCLUSION

A new type of stable cluster  $\text{Al}_n\text{H}_{3n}$  that obeys the concept of super-atom is predicted from first principles calculations. It could be another important aluminum hydride family for rich hydrogen phase apart from the well-known Wade-Mingos clusters  $\text{Al}_n\text{H}_{n+2}$ . A simple structural consideration for such new clusters is revealed, which requires an aluminum core-frame that can provide  $n$  vertexes and  $2n$  Al–Al edges to bond hydrogen atoms. Detailed electronic structures of these new clusters have been given and illustrated with interesting atomic orbital pictures. It is found that these new clusters can form stable polymeric chain structures without causing any structural modifications. With high hydrogen percentage per molecular and very high combustion heat, these stable hydrogen rich clusters could be useful for energy applications.

#### V. ACKNOWLEDGEMENTS

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