

# Structures and stability of $\text{Al}_7\text{C}$ and $\text{Al}_7\text{N}$ clusters

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**Abstract.** We report results of the atomic and electronic structures of  $\text{Al}_7\text{C}$  cluster using *ab initio* molecular dynamics with ultrasoft pseudopotentials and generalized gradient approximation. The lowest energy structure is found to be the one in which carbon atom occupies an interstitial position in  $\text{Al}_7$  cluster. The electronic structure shows that the recent observation [Chem. Phys. Lett. **316**, 31 (2000)] of magic behavior of  $\text{Al}_7\text{C}^-$  cluster is due to a large highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gap which makes  $\text{Al}_7\text{C}^-$  chemically inert. These results have further led us to the finding of a new neutral magic cluster  $\text{Al}_7\text{N}$  which has the same number of valence electrons as in  $\text{Al}_7\text{C}^-$  and a large HOMO-LUMO gap of 1.99 eV. Further, calculations have been carried out on  $(\text{Al}_7\text{N})_2$  to study interaction between magic clusters.

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## 1 Introduction

The discovery of magic numbers in alkali metal clusters [1] started a new era in cluster science. The large abundance of sodium clusters with 2, 8, 20, 40... atoms in these experiments was proposed to have the same origin as the magic numbers in nuclei. Following the analogy of the nuclear shell structure, the magic numbers in alkali metal clusters were attributed to be due to the electronic shell structure. Similar to the bulk, the valence electrons of alkali atoms could be considered to be delocalized in the volume of the cluster and move in the weak (pseudo) potential of the ion-cores which could be approximated by a spherical jellium potential. The electronic levels in this potential are quantized according to the spherical orbitals, leading to the well-known electronic shell structure. Accordingly clusters with closed electronic shells are very stable and behave as superatoms very similar to the rare gas atoms. This idea had attracted much attention as it could lead to a novel class of materials with superatoms as the building blocks. As there could be many possibilities of developing such clusters with differing properties, it is hoped to pave a way for tailor-made materials.

The interesting aspect of such superatoms is that the effective number of valence electrons of a cluster can be altered either by changing their size or composition. It is, therefore, possible not only to mimic the electronic

configuration of an atom in the periodic table but also to explore new possibilities which could hitherto not be permitted with atoms as the building blocks. The ability to alter the composition and size at will provides an unprecedented opportunity to design clusters as superatoms. A typical example for this is found in aluminum clusters. Bulk aluminum is a nearly free electron metal. However,  $\text{Al}_{13}$  cluster behaves like a chlorine atom with nearly the same electron affinity. It has a total of 39 valence electrons which are one short of the  $2p$  shell closing. This cluster, therefore, interacts strongly with alkali atoms [2]. Also when doped with C or Si,  $\text{Al}_{12}\text{Si}$  with 40 valence electrons become much more stable [3,4] than  $\text{Al}_{13}$  with a large HOMO-LUMO gap. This kind of enhanced stability has also been theoretically found for  $\text{Al}_{19}$  and  $\text{Al}_{23}$  by doping with Si recently [5].

Experimental confirmation for such doped magic clusters is very crucial for future developments. Recently Leskiw and Castleman [6] have reported a large abundance of  $\text{Al}_7\text{C}^-$  cluster and its non-reactive nature with oxygen. They proposed a structure of this cluster as an  $\text{AlC}^-$  dimer interacting with  $\text{Al}_6$  cluster. Its stability was proposed to be due to the closed shell nature of  $\text{Al}_6$  with 18 valence electrons and of  $\text{AlC}^-$  with 8 valence electrons. However, here we show that this is not the case and that carbon interacts with  $\text{Al}_7$  strongly occupying the interstitial position. The electronic structure of this cluster is used to explain the magic nature of  $\text{Al}_7\text{C}^-$ . Further, considering the equivalence of  $\text{C}^-$  with N, we expected neutral  $\text{Al}_7\text{N}$  to be magic. This is indeed confirmed by the present

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**Table 1.** The geometric and electronic parameters for  $\text{Al}_7$ ,  $\text{Al}_7\text{C}$  and  $\text{Al}_7\text{N}$  clusters.  $\epsilon$  is the binding energy (eV/atom),  $R_m$ , the mean bond length between Al atoms,  $E_g$ , the HOMO-LUMO gap (eV), and SM, the spin multiplicity.

cluster	symmetry	$\epsilon$	HOMO	LUMO	$E_g$	SM	$R_m$
$\text{Al}_7$	$C_{3v}$	2.15	$a_1 \uparrow$	$a_1 \downarrow$	0.7159	2	2.7198
$\text{Al}_7\text{C}$	$C_{2v}$	2.927	$a_1 \downarrow$	$a_1 \uparrow$	0.3355	2	2.855
$\text{Al}_7\text{N}$	$C_{3v}$	3.30	$e$	$a_1$	1.99	1	2.872

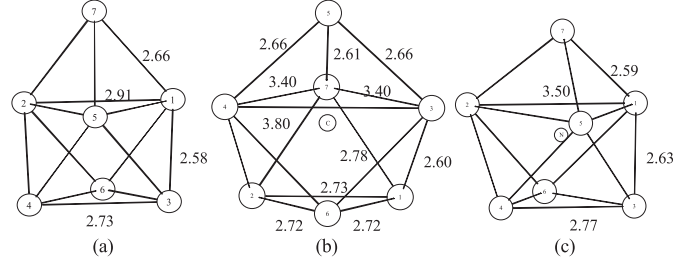
calculations which predict  $\text{Al}_7\text{N}$  to be isostructural with  $\text{Al}_7\text{C}$  but with a higher symmetry due to its closed shell electronic configuration. Clusters of aluminum nitride are interesting because it is an important wide band gap semiconductor for optoelectronic devices and is one of the best known thermal conductors with partly ionic and partly covalent bonding [7]. We, therefore, also performed calculations on a dimer of  $\text{Al}_7\text{N}$  to study interactions between such magic clusters.

In Section 2 we present the computational details while the results and a discussion is given in Section 3. Finally our conclusion is given in Section 4.

## 2 Theoretical method

We use the *ab initio* molecular dynamics method [8] based on the density functional theory (DFT) which has now become a well established tool to study structural properties of materials. In particular the plane wave basis and pseudopotential method provide a simple framework in which the calculation of Hellmann-Feynman force is greatly simplified so that extensive geometry optimization is possible. However, for carbon and nitrogen, the lack of corresponding core states for orthogonalization makes the tightly bound  $2p$  valence wave functions sharply peaked. As a result, in the conventional pseudopotential scheme [8], a relatively hard pseudopotential has to be generated and a relatively large number of plane-wave basis functions are needed in the calculations. This makes the study of structural optimization of clusters containing carbon and nitrogen quite difficult. In the present calculations we use the Vienna *ab initio* simulation code [9–11] based on the ultrasoft pseudopotentials [12] and a plane-wave basis. This uses the finite-temperature density functional theory of Mermin [13] so that the variational quantity is the electronic free energy. The finite temperature leads to the broadening of the one electron levels and helps to improve the convergence of Brillouin-zone integrations.

The minimization of the free energy over the atomic and electronic degrees of freedom is performed using the conjugate gradient iterative technique [14]. We use a simple cubic supercell with 15 Å edge length for a single cluster, and 28 Å for a cluster dimer. In such a big supercell only the  $\Gamma$  point is used to represent the Brillouin zone. The exchange-correlation energy is calculated within the generalized gradient approximation [15] (GGA) with spin-polarization. The calculations are performed with high precision using a cut-off of 170 eV, 373 eV and 435 eV for pure Al cluster, dopping with C and N clusters, respectively. The convergence criteria for energy and force



**Fig. 1.** Optimized structures of (a)  $\text{Al}_7$ , (b)  $\text{Al}_7\text{C}$ , and (c)  $\text{Al}_7\text{N}$ .

are  $10^{-5}$  eV and  $0.001 \text{ eV}/\text{\AA}$ , respectively. The structure optimization is symmetry unrestricted.

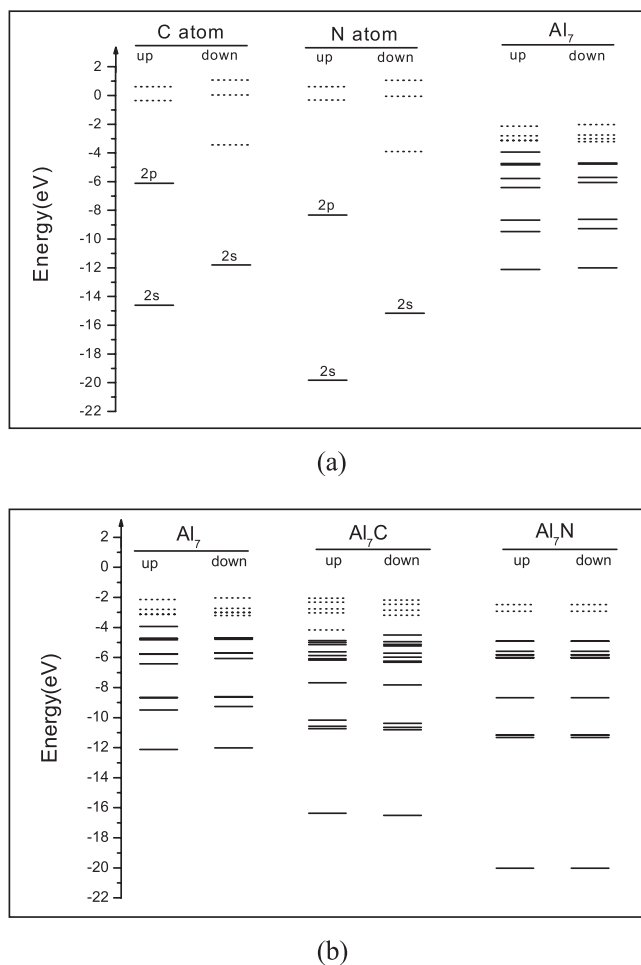
## 3 Results and discussions

As a test we first carried out calculations on  $\text{Al}_2$ . The ground state is found to be  $^3\Pi_u$  with bond length of 2.48 Å and binding energy of 1.86 eV. These are in good agreement with the values obtained from other theoretical results [16] as well as the experimental value [17] of the binding energy (1.5 eV). In the following we discuss results on  $\text{Al}_7\text{C}$  and  $\text{Al}_7\text{N}$  clusters as well as the  $\text{Al}_7\text{N}$  dimer. The binding energies, HOMO-LUMO gaps and the mean bond lengths for  $\text{Al}_7$ ,  $\text{Al}_7\text{C}$  and  $\text{Al}_7\text{N}$  clusters are given in Table 1.

### 3.1 $\text{Al}_7\text{C}$

The high stability of  $\text{Al}_7\text{C}^-$  cluster was explained in reference [6] within a jellium model. According to their interpretation  $\text{AlC}^-$ , a stable eight electron entity and  $\text{Al}_6$  with  $1d$  closed shell in jellium model combine to form  $\text{Al}_7\text{C}^-$ , *i.e.*  $\text{AlC}^- + \text{Al}_6 \rightarrow \text{Al}_7\text{C}^-$ . However, this explanation is not sound as we show in the following.

We consider neutral  $\text{Al}_7$  and  $\text{Al}_7\text{C}$  clusters to understand the large abundance of  $\text{Al}_7\text{C}^-$ . The most stable structure of  $\text{Al}_7$  is found to be a capped antiprism with  $C_{3v}$  symmetry as shown in Figure 1a. A similar result was obtained using the local spin density approximation (LSDA) by Jones [16] and the local density approximation by Kumar [18]. The bond length in the upper (lower) triangle is 2.91 Å (2.73 Å) and the nearest neighbor interatomic distance between the triangles is 2.58 Å. The bond length between the capping atom and the upper triangle is 2.66 Å. The average binding energy per atom is 2.15 eV. This is significantly lower than the LSDA value [16]. The



**Fig. 2.** Electron energy levels for (a) C atom, N atom and  $\text{Al}_7$  and (b)  $\text{Al}_7\text{C}$ , and  $\text{Al}_7\text{N}$  clusters. The solid lines are for the occupied states and dotted lines for the unoccupied states. There is a large gap between the first and the next LUMO states of  $\text{Al}_7\text{C}$  which should make  $\text{Al}_7\text{C}^-$  magic. Also a large HOMO-LUMO gap is clearly seen for  $\text{Al}_7\text{N}$ .

energy spectrum (Fig. 2a) of  $\text{Al}_7$  can be described within the jellium model such that  $1s$ ,  $1p$ ,  $1d$  and  $2s$  up- and down-spin states are fully occupied and the remaining electron occupies the lowest lying  $a_1$  up-spin state derived from the  $1f$  level. The LUMO is  $a_1$  down-spin state and the HOMO-LUMO gap is 0.716 eV.

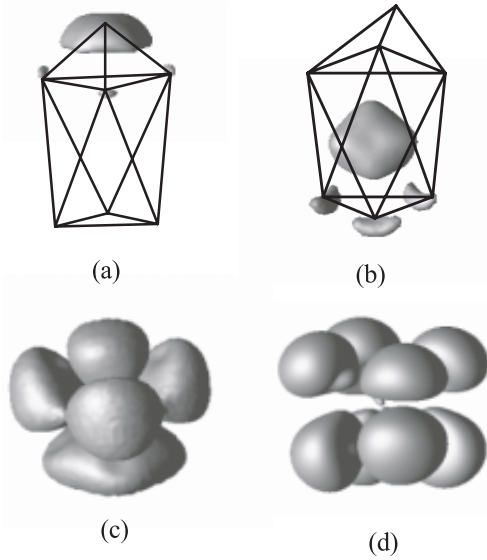
For  $\text{Al}_7\text{C}$  we tried several configurations: C on the top of the capping Al atom as well as on bridge and hollow sites with nonequivalent positions. The top site is found to be a local minimum, while for all other configurations, C atom penetrates into the  $\text{Al}_7$  cluster to occupy the interstitial position. This is lower in energy than the top site position. The converged structure has  $C_{2v}$  symmetry as shown in Figure 1b. Note that the carbon atom is not at the center of the  $\text{Al}_6$  antiprism but slightly displaced upwards so that the distance between the C and the capped Al atoms is 2.07 Å. This also gives rise to an increase in the interatomic distances in the upper triangle of  $\text{Al}_7$ . The binding energy increases significantly

(2.927 eV/atom) due to strong interactions between the  $2p$  orbitals of C with those of  $\text{Al}_7$ . As the total number of valence electrons is odd, there are slight distortions which lift the degeneracy of the states. The electronic structure of this cluster can be understood by considering interaction of a carbon atom with  $\text{Al}_7$ . From the energy spectra of  $\text{Al}_7$  and C (Fig. 2a), it is seen that the  $2s$  level of carbon lies deep in energy below the spectrum of  $\text{Al}_7$  and even after interaction there is a deep level at around  $-16$  eV (Fig. 2b). Therefore, this level is associated primarily with the carbon atom. The  $2p$  state of carbon lies within the spectrum of  $\text{Al}_7$  and should interact strongly. The 3 states around  $-10$  eV are associated with  $\text{Al}_7\text{C}$  complex and the remaining spectrum could be described such that the complex of  $1d$  orbitals is partially occupied with one hole. The physical picture for  $\text{Al}_7\text{C}^-$  is one in which there is charge transfer from the  $1f$  state of  $\text{Al}_7$  to carbon and strong interactions between the  $2p$  states of carbon and the  $2s$  state of  $\text{Al}_7$  making  $1d$  state as the frontier orbital. Thus in the neutral  $\text{Al}_7\text{C}$  cluster there is a hole in the  $1d$  state. In the spin-polarized calculation this leads to only a small HOMO-LUMO gap of 0.336 eV followed by a larger gap. For negatively charged  $\text{Al}_7\text{C}$  cluster, the additional electron occupies this hole giving rise to a large HOMO-LUMO gap and the stability of this cluster. In the following we now consider the case of  $\text{Al}_7\text{N}$  and show that this is in fact the case.

### 3.2 $\text{Al}_7\text{N}$

As discussed above, the hole in the  $1d$  state of  $\text{Al}_7\text{C}$  can be occupied by the additional electron in N so that  $\text{Al}_7\text{N}$  should have a closed electronic shell configuration. The lowest energy structure of  $\text{Al}_7\text{N}$  is found to be similar to  $\text{Al}_7\text{C}$  but with a higher symmetry ( $C_{3v}$ ) as shown in Figure 1c. The distance between N and the capped Al atom is 2.12 Å. The distances from N atom to the atoms in upper and down triangles are 2.08 and 2.106 Å, respectively. These are comparable to the Al-N bond length (1.89 Å) in bulk AlN as well as (1.83 Å) in  $\text{Al}_3\text{N}$  cluster with centered triangular configuration. The latter is also found to be a very stable cluster [19]. The binding energy in  $\text{Al}_7\text{N}$  increases further to 3.30 eV/atom. Strong interactions take place between the  $2p$  orbitals of N with the  $1p$  states of  $\text{Al}_7$  (see Fig. 2a). The overall spectrum of  $\text{Al}_7\text{N}$  is similar to that of  $\text{Al}_7\text{C}$  but it is more compact due to higher symmetry. The  $2s$  level of N lies further deeper, as shown in Figure 2b. The spin multiplicity is found to be 1 due to the closed shell electronic configuration. The HOMO is doubly degenerate  $e$  state while the LUMO is  $a_1$  with a large HOMO-LUMO gap of 1.99 eV. This should make this cluster to be strongly stable and abundant.

The electronegativity of nitrogen is higher than that of Al atom whereas the ionization potential of  $\text{Al}_7$  is lower than that of Al atom. Therefore, some charge transfer should be expected to N from the rest of the cluster. As the capping Al atom is less coordinated, the frontier orbital of  $\text{Al}_7$  is more localized around it. It was shown [18] that a chlorine atom has the top site to be of lowest energy due



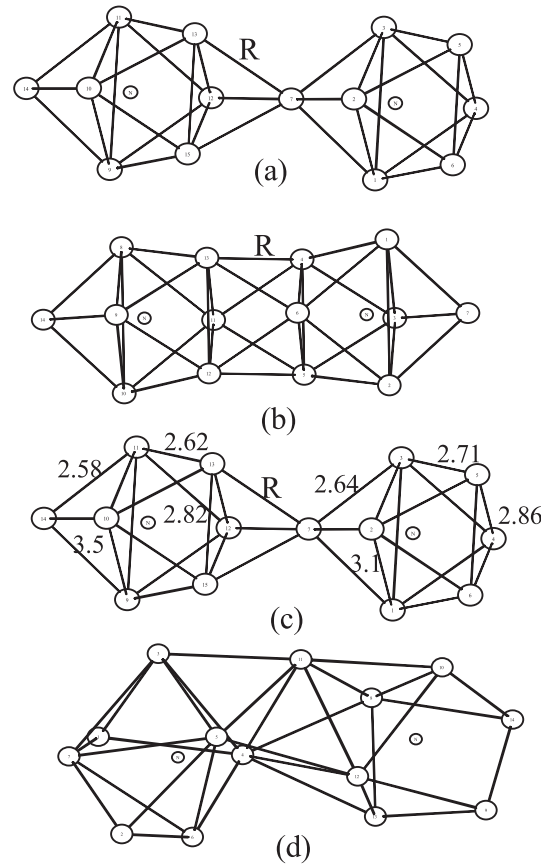
**Fig. 3.** Constant electronic charge density surfaces of  $\text{Al}_7\text{N}$  cluster for (a) depletion and (b) excess of charge as compared to the overlapping densities of  $\text{Al}_7$  and N. (c) and (d) show the surfaces for the HOMO and LUMO states in  $\text{Al}_7\text{N}$ . The values of charge in the four cases are 0.036, 0.02, 0.01, and 0.006 electrons/ $\text{\AA}^3$ , respectively.

to charge transfer from this state. Thus when a nitrogen atom is added to  $\text{Al}_7$ , charge transfer takes place from this capped Al atom to N atom leading to a short bond length between them. This is also borne out from the charge densities shown in Figures 3a and 3b. The constant density surfaces for the excess and depletion of charge as compared to the overlapping charge densities of  $\text{Al}_7$  and N at the respective ionic positions in  $\text{Al}_7\text{N}$ , show that the capping as well as the three Al atoms in the upper triangle lose electrons, while N and the other three Al atoms in the lower triangle have excess of electrons. This leads to an ionic character of bonding in  $\text{Al}_7\text{N}$  cluster. The total charge densities for the HOMO and the LUMO are plotted in Figures 3c and 3d. The HOMO displays features of hybridized  $p$  and  $d$  orbitals while the LUMO exhibits the character of  $1f$  orbitals. This confirms the interpretation given above for  $\text{Al}_7\text{C}$ . The overall features of the bonding appear to be similar to the one found in bulk  $\text{AlN}$ . A similar conclusion was reached by Nayak *et al.* [19] in their study of small  $\text{Al}_n\text{N}$  ( $n \leq 6$ ) clusters.

### 3.3 $\text{Al}_7\text{N}$ dimer

The HOMO-LUMO gap in  $\text{Al}_7\text{N}$  is large and similar [5] to the case of  $\text{Al}_{12}\text{Si}$ . It has been shown that  $\text{Al}_{12}\text{Si}$  can form stable solid [20]. Therefore, it is of interest to study interactions between  $\text{Al}_7\text{N}$  clusters.

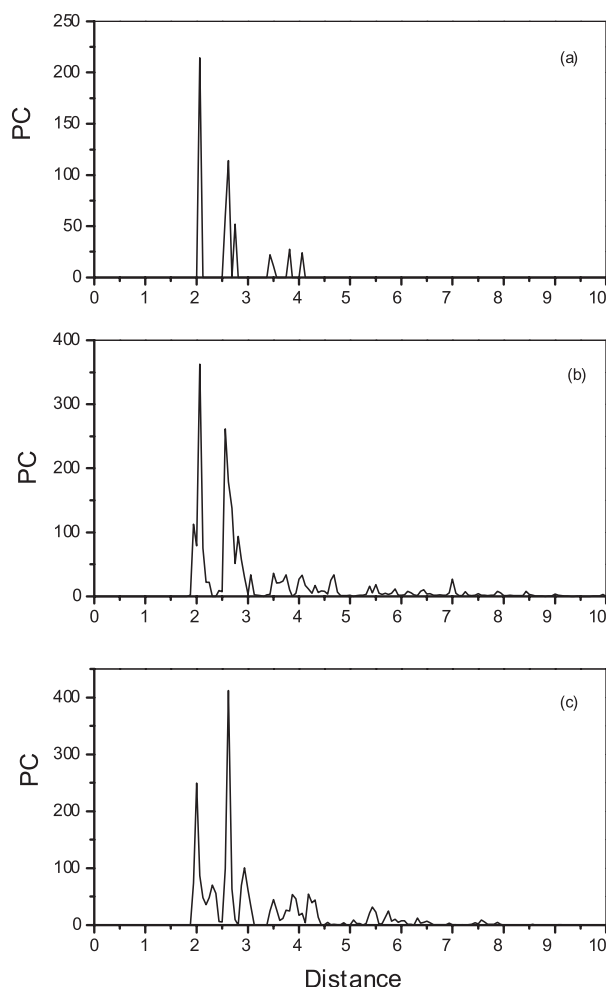
There are many possibilities for the relative orientation of two  $\text{Al}_7\text{N}$  clusters. However, from the structural features of  $\text{Al}_7\text{N}$  cluster itself, we can find the most probable orientations. Here, we consider two configurations as indicated in Figure 4. In the first one (labeled as



**Fig. 4.** Structures of  $\text{Al}_7\text{N}$  dimer with initial configurations (a) 1 and (b) 2. The corresponding optimized configurations are given in (c) and (d), respectively.

configuration 1 in Fig. 4a), the dimer is formed by bottom to top connections of the  $\text{Al}_7\text{N}$  clusters such that atom 7 becomes the common vertex for triangle capping and a centered antiprism is formed. The second one (labeled as configuration 2 in Fig. 4b) is constructed by bottom to bottom contact with a rotation of 60 degrees relative to one another. This also forms an antiprism.

In order to make the two clusters interact strongly, the initial nearest atomic distance  $R$  between the two clusters is set to be 2.5  $\text{\AA}$ , much smaller than the value in  $\text{Al}_7$ . However, after optimization, for configuration 1,  $R$  increases to 2.90  $\text{\AA}$  and the identity of the individual  $\text{Al}_7\text{N}$  cluster remains intact. The cluster still has the original symmetry, as shown in Figure 4c. This is also confirmed from the pair correlation function shown in Figure 5. It is clear that this has nearly the same features for  $\text{Al}_7\text{N}$  cluster and configuration 1 of the dimer. The total binding energy between the clusters is only 0.557 eV, while the HOMO-LUMO gap decreases to 0.745 eV. With this configuration, it could be possible to design a one dimensional cluster array like a nano quantum wire. In configuration 2 there is much stronger interaction and the net gain in energy is 1.40 eV. The nearest interatomic distance  $R$  between the two clusters is 2.68  $\text{\AA}$  which is shorter than in the case of configuration 1. Also, there is significant distortion in the original



**Fig. 5.** Pair correlation (PC) functions (in arbitrary unit) for (a)  $\text{Al}_7\text{N}$  cluster, and optimized cluster dimer with (b) configuration 1 and (c) configuration 2. The distance is in Å.

structure of the two clusters, which is reflected in the pair correlation function in Figure 5c.

The final structure is given in Figure 4d. It appears that the non-spherical shape (low symmetry) of this cluster makes many possibilities to interact and easy to aggregate. Therefore, in order to synthesize cluster assembled materials, it seems important not only to have clusters with a large HOMO-LUMO gap but also a high symmetry of structure.

## 4 Summary

In summary, we have studied the atomic and electronic structures of  $\text{Al}_7\text{C}$  and  $\text{Al}_7\text{N}$  clusters using *ab initio*

calculations based on the ultrasoft pseudopotential scheme and explained the stability of the observed magic behavior of  $\text{Al}_7\text{C}^-$ . The present results lead to a different structure as well as interpretation than anticipated in the experimental work. Further, we have found a new magic cluster,  $\text{Al}_7\text{N}$ , with a large HOMO-LUMO gap of 1.99 eV. However, due to the nonspherical shape, the interaction between  $\text{Al}_7\text{N}$  clusters depends on the relative orientation. It, therefore, appears that a proper control of the size, composition and shape at the atomic level could lead to a synthesis of new cluster based materials.

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