# *Ab initio* molecular dynamics studies of metal clusters

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**Abstract.** We present results of our *ab initio* molecular dynamics simulations on the atomic and electronic structure of clusters of divalent metals, aluminum and antimony, which exhibit a range of bonding characteristics e.g. non-metal–metal transition, metallic and covalent respectively. Results of these studies have been used to develop icosahedral $Al_{12}X$ (X = C, Si and Ge) superatoms with 40 valence electrons which correspond to a filled electronic shell. It is found that the doping leads to a large gain in the binding energy as compared to $Al_{13}$, suggesting this to be a novel way of developing species for cluster assembled materials. Further studies of adsorption of Li, Si and Cl atoms on $Al_7$ and $Al_{13}$ clusters show marked variation in the adsorption behaviour of clusters as a function of size and the adsorbate. Silicon reconstructs both the clusters and induces covalency in Al–Al bonds. We discuss the adsorption behaviour in terms of the superatom–atom interactions.

**Keywords.** *Ab initio* molecular dynamics; metal clusters; adsorption.

## 1. Introduction

Studies on clusters of several elemental as well as binary metals show a large variation with size in ionization potential (Whetten *et al* 1985; Nakajima *et al* 1991), chemisorption behaviour (Whetten *et al* 1985; Leuchtner *et al* 1989) and magnetic moments (Billas *et al* 1994) etc. Since this could lead to a novel way of developing nanomaterials with desired properties (Kumar 1996; Palmer 1997; Perez *et al* 1997), much interest has been aroused in understanding the evolution of materials properties with size. The gross features of the size dependence of the electronic properties of metal clusters have been understood using a spherical jellium model (de Heer *et al* 1987). Similar to the shell model of nuclei, the eigen states in this jellium model are arranged in the order $1s, 1p, 1d, 2s, 1f, 2p, 1g, 2d, \ldots$ and their successive filling leads to stable clusters with 8, 20, 40, ... valence electrons, which correspond to the closure of an electronic shell. This model thus explains the occurrence of magic clusters with 8, 20 and 40 valence electrons for Na in the mass spectrum (Knight *et al* 1984) as well as the variation in the ionization potential (Ekardt 1984) etc. However, there are many properties of clusters which require treatment beyond the jellium model. Clusters of divalent metals show a non-metal–metal transition as a function of size, whereas the magnetic properties as well as adsorption behaviour are in general structure sensitive. Furthermore, a jellium model may be too simplistic to have a proper understanding of chemisorption or alloying behaviour of clusters and to treat clusters of transition metals and semiconductors. Among the various atomistic approaches used to study the structure and electronic properties of clusters, the one based on the *ab initio* molecular dynamics (Car and Parrinello 1985) with simulated annealing has been particularly

successful (Kumar 1994). Here we present a brief account of our results on various metal clusters as well as studies of adsorption behaviour on aluminum clusters. Section 2 gives the computational details whereas the results are presented in §3. Our conclusions are given in §4.

## 2. Computational method

We have used the *ab initio* molecular dynamics method (Car and Parrinello 1985; Kumar 1994) within the local density functional theory and a plane wave basis formulation. The cluster is placed in a large cell with periodic boundary conditions so that the interaction between the cluster and its images is negligible. The electron–ion interaction is treated using the norm-conserving pseudopotentials (Bachelet *et al* 1982; Stumpf *et al* 1990) in the Kleinman and Bylander (1982) separable form. The Brillouin zone is represented by the $\Gamma$ point for the **k**-space integration. More details of this method can be found in Kumar (1994).

## 3. Results

### 3.1 *Clusters of divalent metals*

Dimers of divalent elements are weakly bonded, but in bulk these are good metals. Therefore, a transition takes place from non-metallic to metallic bonding as the size of cluster grows. We have studied (Kumar and Car 1991) the atomic and electronic structure of magnesium clusters having up to 13 atoms. It has been found that a few bonds in a cluster first get metallic character as the size increases rather than the cluster as a whole. Further, as compared to the well known icosahedral structure of 13-atom van der Waals bonded clusters, $Mg_{13}$ has a structure which can be described as a tricapped trigonal prism interacting with a bent rhombus. A relaxed fragment of the hexagonal closed packed structure is nearly degenerate with this structure which was obtained from simulated annealing. This clearly shows that the metallic nature prevails at this size range though the binding energy is significantly smaller (about 0·9 eV/atom for $Mg_{13}$) than its bulk value (1·69 eV). Clusters with 4 and 10 atoms are magic. The latter again supports a metallic bonding nature in these clusters as 10-atom cluster is not particularly magic for van der Waals-bonded systems. The magic clusters are found to have a large gap between the highest occupied and the lowest unoccupied molecular orbital (HOMO–LUMO) states as well as very low self-adsorption energies. This is in agreement with the experimental observations (Leuchtner *et al* 1989) of oxygen interaction with aluminum clusters according to which magic clusters of aluminum are non-reactive.

A 13-atom calcium cluster behaves (Kumar, to be published) similar to $Mg_{13}$. In contrast experiments (Rayane *et al* 1989) on barium clusters show a 13-atom cluster to be magic. The abundance spectrum (Brechignac, private communication) for Sr clusters does not show 13-atom clusters to be particularly magic but some other features resemble with those of the mass spectra of rare gas clusters. We (Qureshi and Kumar, unpublished) have done a detailed study of Sr clusters and find the

icosahedral structure to be stable for $Sr_{13}$ which was not the case for $Mg_{13}$ or $Ca_{13}$. We find that the $1f$ state of the jellium model splits into a 3-fold and a 4-fold state in the icosahedral structure. The 3-fold state is occupied and there is a HOMO-LUMO gap of about 0·5 eV, leading to the stability of this structure.

## 3.2 *Aluminum clusters*

Aluminum clusters have been the subject of several studies as aluminum is a classic example of $s-p$ bonded metals which are theoretically simpler to treat than the technologically more important transition metals. Aluminum serves a very good model to understand the behaviour of $s-p$ electrons in metals as well as in clusters. Moreover, aluminum is adjacent to silicon, boron and gallium which exhibit directional bonding. Often, there is a change in the bonding character of a cluster as compared to bulk. It would be of interest to know if aluminum clusters would show a bonding different from the metallic one. We have carried out *ab initio* molecular dynamics simulations on a few selected structures of aluminum clusters. These studies have been done to further understand the chemisorption behaviour on metal clusters. We used a plane wave expansion with 11·5 Ry cut-off and the $s$ component of the norm-conserving pseudopotential was treated as non-local. We used a face centred cubic cell of lattice constant 38·5 a.u. The structures of some selected clusters are shown in figure 1. The binding energies are given in table 1. Our results are in agreement with those obtained by Jones (1991) using the spin polarized local density functional theory according to which low-spin configurations are energetically more favourable in this size range, and also with those of Yi *et al* (1991) for the 13-atom cluster which is a slightly distorted icosahedron. The binding energy tends to approach the bulk value much faster as compared to the
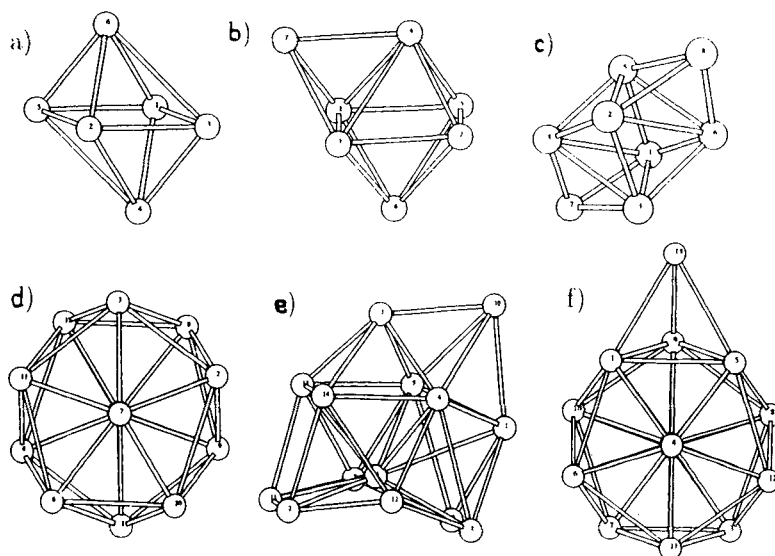


**Figure 1.** Calculated structures of $Al_n$ clusters. (a)-(d) correspond to $n = 6$, 7, 8 and 13. (e) and (f) are two isomers of $Al_{14}$. (f) is of lower energy.

**Table 1.** Binding energies of Al$_n$ clusters.

| Cluster | BE (eV) |
|---------|---------|
| Al$_6$  | 2·32    |
| Al$_7$  | 2·52    |
| Al$_8$  | 2·58    |
| Al$_{13}$ | 2·89  |
| Al$_{14}$ | 2·93  |

divalent metal clusters. For 6-atom cluster the structure is an octahedron. For 7-atom cluster, the one shown in figure 1b, has the lowest energy but a capped prism is nearly degenerate. The 8-atom cluster is obtained by capping a face of the 7-atom cluster. For the 14-atom cluster, the structure (figure 1f) with an Al atom interacting with a 13-atom icosahedral cluster has the lowest energy. We have also studied a configuration obtained for Si on Al$_{13}$ (figure 1e and discussion below) and it is about 0·2 eV higher in energy than the one shown in figure 1f. This appears to have a covalent bonding character and is, therefore, of interest in understanding the behaviour of aluminum clusters.

### 3.3  *Clusters of antimony*

The mass spectrum of antimony clusters obtained from thermal evaporation (Sattler *et al* 1981) shows abundance of Sb$_{4n}$ (*n*, an integer) at low temperatures and is different from the one obtained for clusters of isovalent bismuth. On the other hand, laser evaporation (Geusic *et al* 1988) led to the abundance of 3-, 5- and 7-atom clusters in both the cases which was not understood. Our studies (Kumar 1993; Sundararajan and Kumar 1995) on antimony clusters show a strong stability of Sb$_4$. For Sb$_8$, a structure with two weakly bonded tetrahedra has the lowest energy but another structure with a bent rhombus interacting with a distorted tetrahedron is marginally higher in energy within the LDA. A bent rhombus structure was also found to play an important role for other clusters. For 3-, 5- and 7-atom clusters we find that the singly occupied HOMO has a large separation from the second highest occupied state. Therefore, positively charged clusters, if assumed to have the same structure, will have a large HOMO–LUMO gap which can explain the abundance of Sb$_3$, Sb$_5$ and Sb$_7$ clusters in the laser ablation spectrum. It is interesting to note that studies (Brechignac *et al* 1995) on charged antimony clusters showed initially fragmentation into 3-, 5- and 7-atom clusters. This sequence then changes for larger clusters. From our calculations, the gap between the second and the highest occupied MO decreases with size and therefore, it suggests that the particular stability of odd clusters should disappear with size in agreement with the fragmentation experiments.

### 3.4  *Adsorption on aluminum clusters*

Studies (Somarjai 1994; Masel 1996) of adsorption on semi-infinite surfaces have shown that the atomic structure, and additives such as Na (promoter), S and P

(poison), affect chemical reactions in a significant way. Much efforts have been devoted to understand this in the past two decades. Clusters have, in general, different structures as compared to the bulk and their electronic structure could be size sensitive. This can lead to changes in the reaction rates by several orders of magnitude as a function of size (Whetten *et al* 1985). Therefore, it is important to understand this interaction as a function of cluster size.

Several studies of adsorption on clusters have been done to model the surface–adsorbate interaction, which is predominantly a local phenomenon. These studies, however, do not include structural changes due to the finite size of a cluster and also, generally, ignore structural rearrangement that may occur upon adsorption. Further, the charge transfer and screening effects in clusters resulting from adsorption are likely to be different as compared to semi-infinite surfaces. These may have important implications for the binding energy, adsorption site etc on clusters. Here we discuss briefly our results of Li, Si and Cl atoms adsorbed on $Al_7$ and $Al_{13}$.

In one of the earliest studies of adsorption on metals, Lang and Williams (1978) studied Li, Si and Cl on a jellium surface with the electron density corresponding to Al. It was shown that the Li atom donates its charge to the surface (an empty resonance) while a Cl atom takes away charge from the surface (fully occupied resonance). Silicon, however, has a covalent bonding and the *s–p* resonance is only partially occupied. Subsequent studies have shown (Norskov 1990) that the contribution of the *s–p* electrons to the binding energy of an adsorbate in a *d*-series is
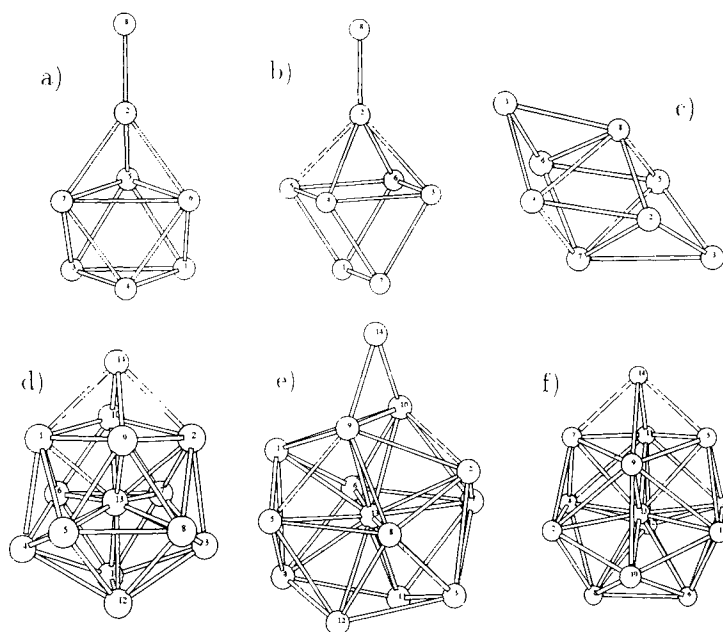


Figure 2. Structures of (a) Li and Cl on the top-site. (b) An isomer of Cl on Al, which is nearly degenerate with (a) and (c) Si on $Al_7$ (atom no. 8). (d) Bridge site for Li and (e) Cl adsorption on $Al_{13}$. (f) Shows the lowest energy structure for $Al_{13}Si$ cluster in which Si is 4-fold coordinated on an otherwise icosahedral $Al_{13}$ cluster. The adsorbate is marked 14 in the figure.

nearly constant. It has been found (Puska *et al* 1981) that for each atom embedded in a homogeneous electron gas, there is an electron density for which the binding energy is maximum. In the effective medium theory of adsorption (Norskov 1990), an adatom tries to find the electron density at the surface corresponding to this optimal binding energy. For clusters, however, we show that this *s–p* electron contribution itself could be quite different depending upon the size due to quantum effects.

We consider $Al_7$ and $Al_{13}$ clusters (Kumar 1997; Kumar, to be published), which have 21 and 39 valence electrons respectively, and are nearly magic in the spherical jellium model (de Heer *et al* 1987) according to which metal clusters with 20 and 40 valence electrons have closed electronic shell configurations similar to rare gas atoms. We can, therefore, consider $Al_7$ and $Al_{13}$ clusters as superatoms with likely properties of an alkali and a halogen atom respectively. The HOMO then represents the valence state whereas the deeper levels, the core.

The adatom was placed on a 3-fold or a bridge site of the $Al_{13}$ cluster and in the case of $Al_7$, on the triangular face of the octahedron opposite to the one on which an aluminum atom was placed (figure 1b). The clusters were fully relaxed
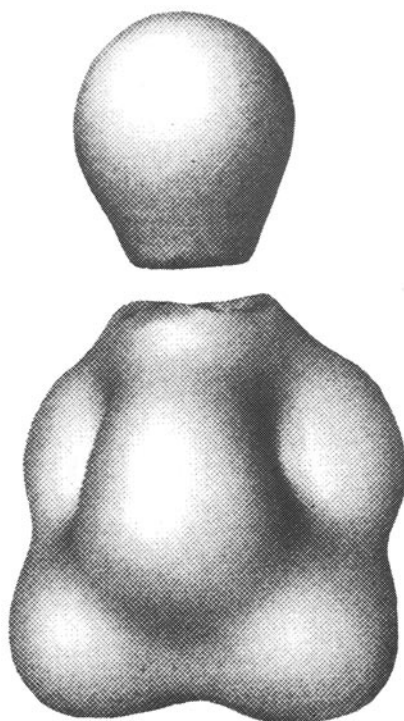


**Figure 3.** The electronic charge density surface for $Al_7Cl$ with the density of $0.023$ e/v. The blob at the top represents density around the Cl ion. The gap between the Cl and $Al_7$ corresponds to low electronic charge density and the bonding is ionic. In the lower portion of the $Al_7$, the charge distribution is similar to the case in metals whereas in the upper part, the charge is more concentrated along the bonds giving rise to covalency in the bonding. *v* is the volume of the primitive cell.

to minimize the energy. For Li and Cl on $Al_7$, however, a top site (figure 2a) is favoured, whereas bridge site is favoured for $Al_{13}$ (figures 2d and e respectively). The isomer with Cl adsorbed on the top site of the capped trigonal prism (figure 2b) is nearly degenerate with the structure shown in figure 2a. Adsorption of silicon leads to reconstruction of both the clusters as shown in figures 2c and 2f. For $Al_7$, Si is bonded with five aluminum neighbours. For $Al_{13}$, the relaxed bridge site, leading to a 4-fold coordination of Si, has the lowest energy among all the structures we have studied. A 3-fold site, analogous to $Al_{14}$, is only $0.027$ eV higher in energy. In this configuration, Si behaves like a metal atom. However, there is another totally different structure analogous to the one shown in figure 1e with the atom 3 replaced by Si. This appears to be a covalently bonded form and lies only $0.136$ eV higher in energy than the lowest energy isomer. Similar to $Al_7Si$, in this structure also, the Si atom is bonded with 5 aluminum neighbours. It may be possible to produce such covalently bonded clusters of aluminum.

Large variation ($\approx 1$ eV) in the binding energy (BE), $E_a$, with cluster size is seen for Li and Cl. In a few cases even the site to site variation of $E_a$ is very large. $E_a$ of Li on a 3-fold site of $Al_7$ cluster is only $0.11$ eV lower than for the top site ($2.2$ eV), whereas for Cl the top site BE ($5.89$ eV) is $1.43$ eV higher than the 3-fold site. Adsorption of Li on $Al_7$ leads to a smaller relaxation of the cluster as compared to Cl. The electronic charge density for $Al_7Cl$ (figure 3) shows that Cl introduces covalency in Al–Al bonds.

Lithium on $Al_{13}$ has a binding energy of $3.3$ eV. The large binding energy of Li on $Al_{13}$ is due to the completion of the $2p$ electronic shell corresponding to the jellium model. The HOMO–LUMO gap is $1.71$ eV, which is more than the value ($1.56$ eV) for $Al_{13}$. The electron charge density for $Al_{13}Li$ cluster (figure 4)
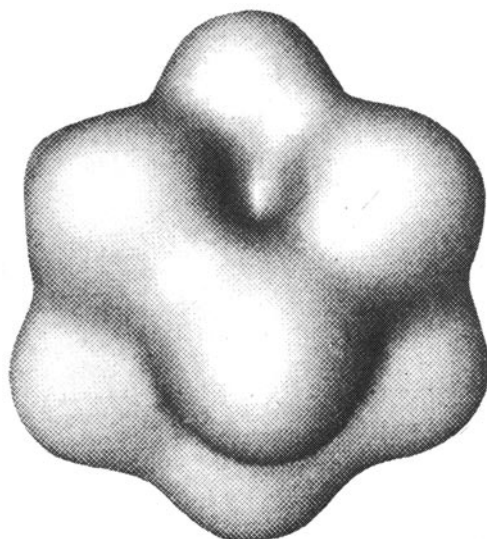


**Figure 4.** The electronic charge density surface for Li on $Al_{13}$ with the density of $0.0195$ e/v. Li is placed at the bridge site where the charge density shows a dip in the figure. All the charge is transferred to $Al_{13}$.

shows that Li gives away its valence electron to $Al_{13}$ cluster, whereas in the case of $Al_7Li$ the charge is shared (Kumar 1997; Kumar, to be published) between Li and $Al_7$.

Chlorine on $Al_{13}$ leads to an expansion of the Al–Al bonds on the opposite side of the adatom (figure 2e). The binding energy is 4·61 eV, which is 1·28 eV smaller than the value for $Al_7$. This trend is in line with the fact that the binding energy of a $Cl_2$ dimer on Al(001) surface is found (Mitsutake *et al* 1995) to be only 4·1 eV. Since Cl poisons chemical reactions and is used for etching aluminum surfaces, our results on Cl interaction with Al clusters could be of help in understanding these processes.

Adsorption of a Si atom leads to a covalent bonding (figure 5) in aluminum. The binding energy, 4·45 and 4·61 eV for Si on $Al_7$ and $Al_{13}$ respectively, is large and changes little as a function of the cluster size. This behaviour is, however, different from $Al_{12}Si$ where a Si atom at the centre of $Al_{12}$ icosahedron stabilizes further the icosahedral cluster with a large binding energy (Khanna and Jena 1992; Gong and Kumar 1993).

## 4. Icosahedral $Al_{12}X$ clusters

$Al_{13}$ cluster has one electron less than the shell filling. Therefore, substitutional doping with a tetravalent atom will make it a 40 valence electron system, and, therefore, a cluster with closed electronic shell configuration. This has been studied by Khanna and Jena (1992) and Gong and Kumar (1993). It was found that the doping leads to a large gain in the binding energy. Our pseudopotential calculations (Kumar and Sundararajan, to be published) show a gain of 2·9 eV with Si substitutional doping. It is also found that a cuboctahedral $Al_{12}Si$ cluster with Si atom
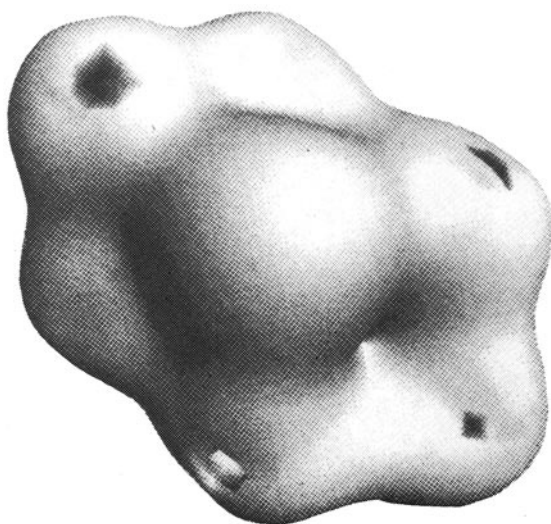


Figure 5. Same as in figure 4 for Si on $Al_7$ with the density of 0·023 e/v. Si (top) is bonded to 3 Al atoms in the upper side and 2 Al atoms below (cf. figure 2).

at the centre, relaxes to the icosahedral structure. Therefore, icosahedral cluster should be very stable. When a Si atom is substituted on a vertex site of the $Al_{13}$ cluster, the binding energy reduces by 0·66 eV, implying the substitution at the centre to be more favourable. Similar behaviour is found for C and Ge. However, doping by tin leads to segregation of Sn atom at the vertex. The segregation energy is 0·42 eV. This is due to the larger size of Sn atom which increases the centre to vertex distance and therefore strains the Al–Al bonds. By segregation to a vertex site, this strain is released. This behaviour is in agreement with the fact that strain energy leads to surface segregation in alloys (Kumar 1979).

## 5. Conclusion

We have presented briefly results of our studies on small clusters of divalent metals, aluminum and antimony as well as adsorption on aluminum clusters using the *ab initio* molecular dynamics method. The nature of bonding in these clusters has been discussed. The adsorption behaviour of aluminum clusters shows significant changes as a function of size due to changes in the electronic structure of clusters. In particular, $Al_7$ with one valence electron outside the shell of 20 electrons behaves like an alkali atom, whereas $Al_{13}$ with one electron less than shell closing, as a halogen. The ionic bonding of Cl with $Al_7$ and Li on $Al_{13}$ thus leads to a larger binding energy as compared to $Al_{13}Cl$ and $Al_7Li$ respectively. Further, by suitable doping, such as in the case of $Al_{12}Si$, clusters can be stabilized in certain structures for developing cluster assembled materials.

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