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1997 J. Phys.: Condens. Matter 9 2859

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Geometries and energies of small aluminium clusters in fcc symmetry

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Received 18 June 1996, in final form 12 November 1996

Abstract. Small aluminium clusters Al_n ($n \leq 8$) as fragments of fcc lattice have been studied from an *ab initio* point of view. Complete geometry optimizations have been carried out at the fourth-order many-body perturbation theory level. Resulting geometric and electronic structure data have been compared with other results available in the literature. Possible clusters have been identified for future studies of chemisorption of different molecules on the aluminium surface. For the (100) surface Al_5 (4, 1, 1) is a 'good' cluster, while for the (110) surface Al_5 (5, 0) appears to be a 'good' cluster. For the (111) surface, Al_8 (3, 3, 2) appears to be an ideal cluster for future studies of chemisorption.

1. Introduction

Recent years have seen an explosive growth [1–7] in the experimental and theoretical studies of atomic and molecular clusters. Novel experimental techniques have been developed to produce clusters of atoms from all types of material for studies under laboratory conditions and important physical and chemical properties have been analysed. Theoretically, several different techniques such as Hartree–Fock formalism, semi-empirical, pseudopotential, and local density calculations are being employed in a concerted effort to understand the properties of clusters. The interplay between experiment and theory has been very intense in this field and has quite often led to new discoveries.

As aluminium is a very common metal and has found many uses in everyday life, clusters of Al atoms have naturally been studied quite extensively through theoretical calculations [8–30] and experiments [31–43]. We briefly discuss four such calculations as the motivations for our work presented here. Using the multireference double-excitation configuration interaction (MRDCI) method, Pacchioni *et al* [12–14] studied chemical bonding and electronic structures of small homonuclear clusters of elements of groups IA, IIA, IIIA, and IVA. For the Al clusters, a pseudopotential basis set [4s4p/2s2p] was used. However, no polarization function was added. The authors claimed that the description of the bond was qualitatively correct and no drastic change in the electronic properties of the cluster was expected with the inclusion of the polarization function. They also noted that the interaction of the 3p atomic orbitals was very important for the stabilization of the cluster and that Al clusters displayed considerable stability even for a small number of atoms. Al_n ($n = 2–5$) clusters were found to have triplet or quadruplet ground states. Upton [17] studied small Al clusters and the interactions of molecular hydrogen with such clusters. In particular, he found that the results of *ab initio* total-energy calculations were different from those

predicted by the electronic shell model. However, a perturbed electron droplet model was found to agree well with the *ab initio* results. Cohesive energies were found to increase with cluster size but did not approach the bulk value with the conventional $n^{-1/3}$ dependence. Bonding was found to be essentially from 3p atomic orbital combinations, in agreement with the results of Pacchioni *et al* [12–14]. Surprisingly, the geometries were three dimensional from Al₄ onwards. On the other hand, from studies of the effects of basis set and correlation on the bond lengths and atomization energies of Al₂ and Al₄, Bauschlicher *et al* [18, 19] and Pettersson *et al* [21] found that polarization functions were very important for adequate descriptions of Al clusters. Inclusion of extensive correlation was also necessary to obtain adequate binding energies but geometries were not significantly affected by correlation. In follow-up studies, they used correlated wave functions and extended basis sets for Al_n ($n = 2-6, 13$) clusters. They also found that Al₄ and Al₅ had planar structures, but Al₆ had a three-dimensional structure. A simplified description using two- and three-body interactions based on Lennard-Jones and Axilrod–Teller potentials was found to agree well with the *ab initio* results. Density functional calculations with simulated annealing have been performed by Jones [25] for Al_n and Ga_n clusters ($n \leq 10$). He found many local minima in the energy surfaces, with a rich variety of structures and spin multiplicities. Transitions from planar to nonplanar structures occurred at $n = 5$, and those to states with minimum spin degeneracy at $n = 6$. Stable structures of larger clusters were found by capping the structures of smaller clusters.

The above results indicate that, even though many results are available in the literature for small Al clusters, strong disagreements exist among different results and no data are available for small clusters in bulk solid state symmetries. In the current work, we present results for geometries and electronic structures of small aluminium clusters as fragments of fcc lattice using *ab initio* many-body perturbation theory up to fourth order. Eventually, these results will be used to study atomic and molecular chemisorption on aluminium metal surface modelled using the information obtained from studies of these small clusters. Using a finite-sized cluster of atoms to model a bulk solid and to study localized properties (e.g. chemisorption) is a difficult problem at best. In the case of simulation of surfaces using the clusters, it becomes even more difficult because the symmetry of the surface exposed to the reactants decides the shape of the clusters chosen to represent the bulk. In particular, the role played by the lower layers must also be included. In the following calculations, these have been suitably accounted for. We note that bulk Al normally exists in fcc structures with a lattice constant of 4.05 Å. We present below results for Al₂–Al₈ clusters in fcc (100, 110, 111) symmetries.

2. Theory

In our calculations, we have used the self-consistent field molecular orbital (MO) theory where the molecular orbitals have been expanded as sums of atomic orbitals (SCF–LCAO–MO). Starting with a set of atoms placed at specific points, the total energy of the cluster has been calculated using the Hartree–Fock approximation. The correlation effect is then included through many-body perturbation theory (MBPT). The many-body perturbation theory used in this work is well documented in the literature [44–46]. We shall, therefore, present only a basic equation to define some terms.

In MBPT, the energy is given by the linked-diagram expansion:

$$\Delta E = E - E_0 = E_{HF} + E_{corr} = \sum_{n=0}^{\infty} \langle \Phi_0 | V [(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_l \quad (1)$$

where Φ_0 is the single-determinant self-consistent field (SCF) wave function, H_0 is the sum of one-electron Fock operators, E_0 is the sum of SCF orbital energies, and $V = H - H_0$ the perturbation, where H is the usual electrostatic Hamiltonian. We have chosen Φ_0 to be the unrestricted Hartree–Fock (UHF) wave function. The subscript l indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from equation (1), the method is usually limited by termination at some order of perturbation theory. In this work, we have carried out complete fourth-order calculations (MP4) which consist of all single-, double-, triple-, and quadruple-excitation terms. After obtaining the total correlated energy for the cluster, the geometry is changed and the energy is calculated again. This is continued until a minimum is found in the energy surface.

3. Computational results and discussions

One of the primary considerations involved in these calculations is the choice of the basis set to be used. Gaussian-type basis sets used in *ab initio* MO computations usually involve some compromise between computational cost and accuracy. As Al is a large system with thirteen electrons, inclusion of all the electrons for an *ab initio* calculation of energy is computationally very expensive. Therefore, the internal electrons of the Al atoms have been represented by Hay–Wadt effective core potentials (ECPs) [47]. The valence electrons have been represented by a scale optimized [3s3p1d/2s2p1d] split basis set. This basis set produces comparable results using a much larger [16s10p1d/4s3p1d] basis set [48]. All the geometries have been optimized at the MP4 level. Therefore, our results are expected to be significantly more accurate than any other results available in the literature.

The clusters were all derived from the basic fcc cell shown in figure 1 by putting atoms at lattice sites with different symmetries. With this symmetry limitation, geometry optimization means the optimization of the lattice constant for the cube. This was performed at the MP4 level of calculation. All the computations were carried out on a Cray YMP 8/864 computer using the Gaussian-92 software [49]. Table 1 lists the bond lengths and the binding energies for the various clusters studied. The binding energy per atom, E_b , for a cluster was calculated using the equation

$$E_b(\text{Al}_n) = [nE(\text{Al}_1) - E(\text{Al}_n)]/n \quad (2)$$

where $E(\text{Al}_1)$ is the energy of a single Al atom and $E(\text{Al}_n)$ is the energy of an Al cluster with n atoms. For bound clusters, the value of E_b is positive. Clearly all the clusters studied are bound. Though our clusters are not free clusters but are fragments of fcc lattice, we first present a detailed comparison of our ‘fcc’ clusters with the free Al clusters presented in the literature.

For Al_2 , an early experimental work of Ginter *et al* [31] found ${}^3\Sigma_g^-$ to be the ground state. A later experiment [32] found the bond length to be 2.46 Å with a bond dissociation energy of 1.55 ± 0.15 eV. Magnetic deflection experiments by Cox *et al* [34] found the aluminium dimer to have a triplet ground state while Cai *et al* [39] found the ${}^3\Pi_u$ to be the ground state of Al_2 from fluorescence excitation spectra. Using different basis sets and different correlation treatments, Bauschlicher *et al* [18] found the $X^3\Pi_u$ to be the ground state with the bond lengths lying between 2.70 and 2.77 Å. The dissociation energies ranged from 1.081 to 1.425 eV. In follow-up studies, using effective core potentials and correlation at contracted CI levels with Davidson correction, Pettersson *et al* [21] found a bond length of 2.75 Å for Al_2 with a bond dissociation energy of 1.20 eV. Pacchioni [12] using a pseudopotential CI method and [4s4p1d/2s2p1d] basis set, also found the ${}^3\Pi_u$ to be the ground state for Al_2 with a bond length of 2.77 Å. Upton [17] found the ${}^3\Sigma_g^-$ and

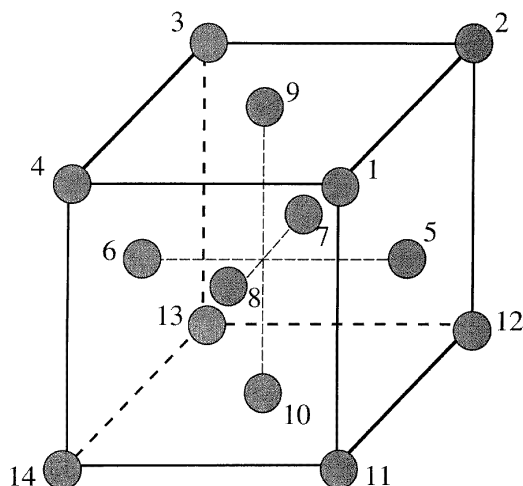


Figure 1. The basic unit for the fcc lattice used in the calculations of the present work.

$^3\Pi_u$ states almost degenerate. However, the $^3\Sigma_g^-$ state was found to be the ground state with a bond length of 2.51 Å and a bond energy of 1.33 eV. Jones [25] found the $^3\Sigma_g^-$ to be the ground state, with a bond length of 2.47 Å. Martinez *et al* [28] have performed density functional calculations using gradient-corrected functionals for Al_n ($n \leq 4$) neutral and cationic clusters. For Al_2 , the ground state was $^3\Pi_u$ at the level of nonlocal spin density approximation of density functional theory but, at the local level, the ground state was $^3\Sigma_g^-$. The energy difference between the $^3\Pi_u$ and $^3\Sigma_g^-$ states was found to be very small. The bond length obtained was 2.73 Å. Martinez and Vela [27], however, quoted a bond length of 2.5 Å for the triplet ground state of Al_2 . This is probably due to the different nature of the gradient corrections. Calaminici *et al* [29] used the same theoretical formalism as that of Martinez and Vale [27] to investigate Al_n , $(Al_n)^+$ and $(Al_n)^-$ ($n = 2-5$) clusters. For Al_2 , the ground state was $^3\Pi_u$ with a bond length of 2.73 Å and a binding energy per atom of 0.91 eV. The empirical many-body potential model of Johnston and Fang [26] found an Al_2 bond length of 2.85 Å and a binding energy per atom of 0.45 eV. Our calculations found the triplet $^3\Sigma_g^-$ state to be the ground state, with a bond length of 2.73 Å and bond dissociation energy of 1.22 eV, as shown in table 1. This verifies that our choice of basis set and computational method are quite acceptable as our results are close to those from the experiment as well as other theories. In this case, the fcc symmetry does not play any role at all because of the small number of atoms involved.

For Al_3 , possible rearrangements of the 3s and 3p nine valence electrons give rise to the low-lying states. However, the nature of the ground state remains controversial, both experimentally and theoretically. On the experimental side, Howard *et al* [33] found a quartet ground state while Cox *et al* [34] and Hamrick *et al* [40] found a doublet ground state. Pettersson *et al* [21] found the ground state to be a 4A_2 state, the geometry being a triangle with a bond angle of 71.0°. Pacchioni and Koutecky [14] found the Al_3 linear structure to be slightly more stable, with a bond length of 2.73 Å. Upton [17] noted that Al_n equilibrium structures were typically derived from the Al_{n-1} parents and that the 2A_1 state was the ground state in all CI calculations. The structure was found to be dominated by π bonding and was almost equilateral with a bond length of 2.62 Å. The bond energies varied between 0.90 and 1.07 eV depending on the type of CI used. Jones [25] found that the

Table 1. A comparison of geometries and binding energies of aluminium clusters.

n Geometry	Bond length (Å)					Binding energy/atom (eV)				
	This work	[18, 19, 21]	[17]	[26]	[28, 29]	This work	[18, 19, 21]	[17]	[26]	[28, 29]
2 Linear	2.73	2.75	2.51	2.85	2.73	0.61	0.60	0.67	0.45	0.91
3 Eq. triangle	2.90		2.62	2.87	2.52	0.79		1.07	0.83	1.42
3 Is. triangle	2.57	2.62/71.0°	2.64/70.3°			0.97	0.92	0.74		
3 Linear chain	2.60	2.62			2.57	0.89	0.78			
4 Rhombus	2.95	2.67			2.56	0.92	1.09		1.03	1.65
4 Square	2.68	2.77	2.61			1.29	0.94	1.12		
		(tetrahedron)	(tetrahedron)							
5 Planar	2.70	2.62			2.61	1.06	1.32			1.85
5 Capped rhombus	2.74					1.29				
5 Capped square	2.77	2.74	2.72			1.45	1.27	1.06		
		(pyramid)	(sq-pyramid)							
6 Eq. triangle	2.69					1.65				
6 Capped planar	2.71					1.47				
6 O _h (cubic)	2.77	2.77	2.78			1.59	1.47	1.22	1.54	
7 Capped eq. tri.	2.74					1.47				
8 Bicapped eq. tri.	2.80					1.31				
8 O _h w/2 cube corners	2.76					2.10				

most stable form of Al₃ was an equilateral triangle with a bond length of 2.46 Å. Martinez *et al* [28] and Calaminici *et al* [29] found a doublet ²A₁ ground state. The geometrical structure was an equilateral triangle with a bond length of 2.52 Å and a binding energy of 1.42 eV/atom at the model core potential level. Johnston and Fang [26] predicted an equilateral triangle for Al₃ with bond lengths of 2.87 Å and a binding energy of 0.83 eV. In our calculations, in different fcc symmetries, we considered an equilateral triangle, a right-angled isosceles triangle and a linear chain for the Al₃ cluster. The isosceles triangle with a ground state of ²A₁ was found to be most stable, with a binding energy of 0.97 eV/atom (see table 1). A full optimization for Al₃ without any fcc constraint yielded a ²A₁ equilateral triangle ground state with a bond length of 2.65 Å and a binding energy of 1.01 eV/atom.

For Al₄, Jones [25] found a planar rhombus to be the most stable structure, in agreement with the results of Pacchioni and Koutecky [14] and Pettersson *et al* [21]. Upton [17] found the tetrahedron to be more stable than the planar square, with a binding energy per atom of 1.12 eV and a bond length of 2.61 Å. He, however, noted that the tendency of free Al clusters was towards fcc substructures and Al₄ was closer to a planar square than the tetrahedral. Martinez *et al* [28] and Calaminici *et al* [29] found the most stable geometry to be a triplet state rhombus with a bond length of 2.56 Å and a binding energy of 1.65 eV. However, Martinez and Vela [27] found a tetrahedron with a quintuplet state to be most stable. Johnston and Fang [26] found the tetrahedron to be 0.13 eV/atom more stable than the planar rhombus. In our fcc symmetry constrained geometries, both the rhombus and the square were studied. The planar square was found to be much more stable than the rhombus. In this case, the binding energy increased from 0.92 eV for the rhombus to 1.29 eV for the square. However, a full optimization for Al without any fcc constraint finds the square and the rhombus almost degenerate in energy, the rhombus being slightly more stable by 0.01 eV/atom.

For the Al₅ cluster, as shown in table 1, we studied three clusters as fragments of fcc lattice. The capped square was found to be the most stable geometry. Pettersson *et al* [21] found a C_{2v} planar structure to be the lowest in energy. Upton [17] found the Jahn–Teller distorted pyramidal structure to be the ground state geometry. The differences might simply

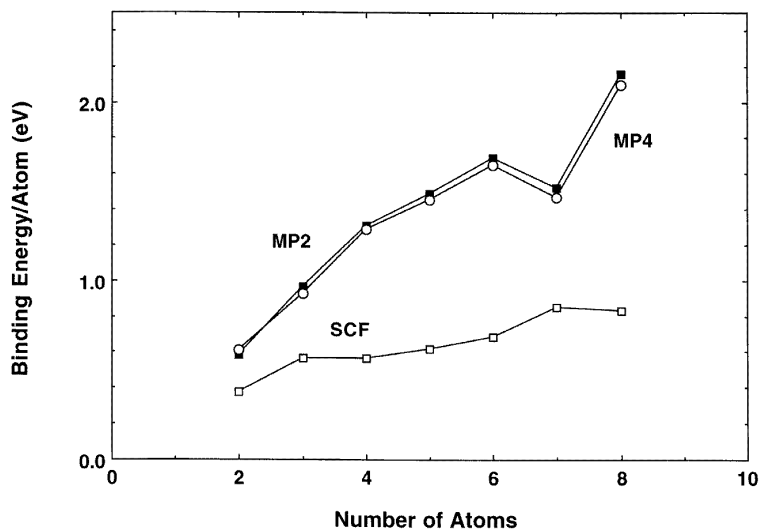


Figure 2. The binding energy per atom for different-sized clusters.

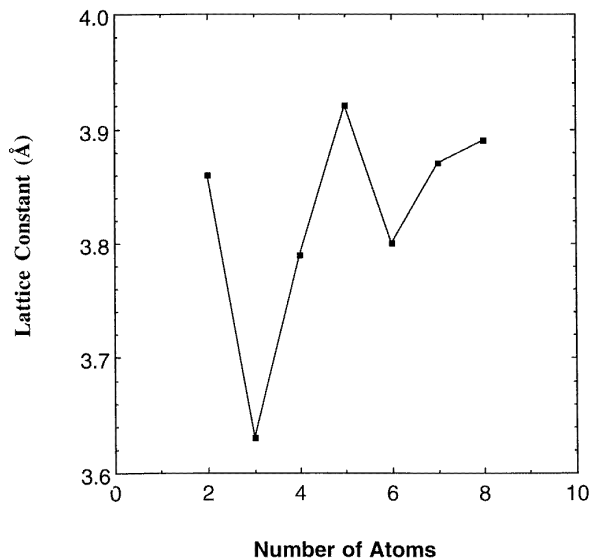


Figure 3. Lattice constants corresponding to different clusters.

be the result of the extent of correlation included in these two sets of calculations. Jones [25] found that a three-dimensional C_s form and a C_{2v} planar structure had almost identical energies. Calaminici *et al* [29] also found a C_{2v} planar structure to be the lowest-energy structure while Johnston and Fang [26] found a trigonal bipyramid with a binding energy per atom of 1.36 eV to be the ground state structure. For Al_6 , we considered three structures, the most stable structure being an equilateral triangle, closely followed by a cubic structure with O_h symmetry. Both Petterson *et al* [21] and Upton [17] found the lowest-energy structure to be the three-dimensional octahedron with O_h symmetry. Pederson [50] found

Table 2. Lattice constants and binding energies per atom for the most stable clusters in different symmetries. The notation used is $Al_n(n_1, n_2, n_3)$, where n_1 , n_2 , and n_3 are the number of atoms in the first, second, and third layers respectively.

Symmetry	Cluster	Lattice constant (Å)	Binding energy per atom (eV)
100	$Al_2(2, 0)$	3.86	0.61
	$Al_3(3, 0)$	3.63	0.97
	$Al_4(4, 0)$	3.79	1.29
	$Al_5(4, 1)$	3.92	1.45
	$Al_6(4, 1, 1)$	3.92	1.59
	$Al_7(6, 1)$	3.87	1.47
	$Al_8(6, 1, 1)$	3.89	2.10
110	$Al_2(2, 0)$	3.86	0.61
	$Al_3(3, 0)$	3.67	0.89
	$Al_5(5, 0)$	3.82	1.06
	$Al_6(5, 1)$	3.80	1.65
111	$Al_2(2, 0)$	3.86	0.61
	$Al_3(3, 0)$	4.10	0.79
	$Al_4(4, 0)$	4.17	0.92
	$Al_5(4, 1)$	3.87	1.29
	$Al_6(5, 1)$	3.84	1.47
	$Al_8(3, 3, 2)$	3.93	1.31

the O_h structure to be the lowest in energy, with a binding energy per atom of 2.45 eV. Johnston and Fang [26] also found the O_h structure to be the lowest in energy, with a binding energy per atom of 1.54 eV. Jones [25] found a Jahn–Teller distorted D_{3d} trigonal antiprism to be the ground state structure, in agreement with the results of Jug *et al* [51].

Our results for the Al_7 and Al_8 clusters are presented in table 1. No other calculations have been reported in the literature for these clusters using Hartree–Fock theory. The density functional calculations of Pederson [50] obtained a binding energy per atom of 2.48 eV for the Al_8 cluster. For Al_7 , Jones [25] found a doublet C_{3v} structure obtained by capping the trigonal antiprism form of Al_6 to be the ground state structure. For Al_8 , he found a ‘cubic’ structure to be the ground state. Both of these states agree with the results of Jug *et al* [51]. Johnston and Fang [26] found a pentagonal bipyramid and a dodecahedron to be the ground state structures of Al_7 and Al_8 , respectively.

To further analyse the results, in figure 2, we have plotted the binding energy per atom against the number of atoms for the most stable clusters. We note that the clusters are bound at all levels of theory. The results for binding energies from MP2 and MP4 calculations are very close; however, the binding obtained with MP4 is slightly less than that with MP2. This behaviour has been observed before for boron clusters [52]. No significant odd–even alternation for the binding energies is observed at the correlated levels of theory. In fact, at the MP2 and MP4 levels, a general monotonic increase is noted, except a dip at $n = 7$. We also observe that out of twenty-two clusters in which our results can be compared with other published data in the literature twelve have better binding energies and four have comparable binding energies (table 1). This is noteworthy considering that our clusters are fcc symmetry constrained and the other results are for ‘free’ clusters. We attribute the better binding energy to the inclusion of correlation at the MP4 level. The largest binding energy of 2.10 eV is obtained at $n = 8$. Since the bulk cohesive energy is 3.39 eV, simple extrapolation indicates that approximately sixteen to twenty atoms are needed to achieve convergence to bulk properties.

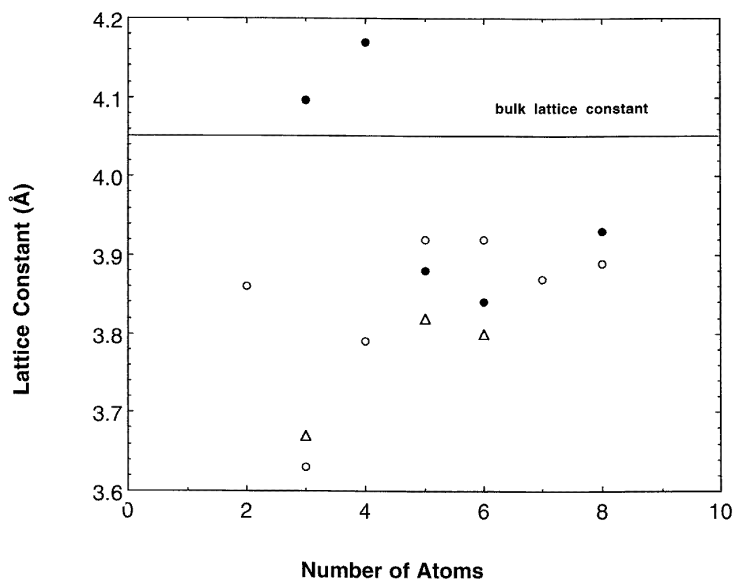


Figure 4. Lattice constant against number of atoms of clusters in different symmetries. The open circles, triangles, and filled circles represent the (100), (110), and (111) surfaces respectively.

As the clusters have been chosen as fragments of fcc lattice, it is possible to define a 'lattice constant' for a small cluster. Depending on the size and the structure of the chosen cluster, it can be produced by placing the atoms on specific sites of an fcc lattice. When this is done for a cluster with optimized geometry, the corresponding lattice constant for the fcc lattice is defined as the lattice constant for the cluster. The lattice constants for the most stable clusters have been plotted in figure 3. Some oscillations are observed up to $n = 7$. Considering that the bulk lattice constant is 4.05 Å and the $n = 8$ cluster has a lattice constant of 3.93 Å, we note again that convergence to the bulk value is much more rapid for the lattice constant than for the binding energy. Such effects have also been observed before for other metallic systems [53].

Table 2 presents the results for the various clusters in different fcc symmetries. The different layers for the atoms noted there can be visualized by a comparison with the structure in figure 1. The quantities presented in table 2 have been plotted in figures 4 and 5. In the (100) surface, there is a general tendency of increasing binding energy as the number of atoms in the different layers increases. In particular, $Al_8(6, 1, 1)$ has a significantly high binding energy. In our previous calculations of chemisorption of hydrogen atoms on Li clusters [54], we found an inverse relationship between binding energy and chemisorption energy. Using the same criterion for Al clusters, it may be said that the Al_8 is not a good site for chemisorption, but $Al_5(4, 1)$ is. Specifically, $Al_5(4, 1)$ is a two-layered cluster with a low binding energy and a lattice constant closest to the bulk lattice constant among all the (100) clusters. For the (110) surface, $Al_5(5, 0)$ appears to be a good site for chemisorption. For the (111) surface, the trends are the same. As the number of atoms in the different layers increases, the lattice constants tend to oscillate but the binding energy, in general, tends to increase. Using the same criterion as before, $Al_8(3, 3, 2)$ should be an ideal cluster for chemisorption studies in the future.

In summary, small aluminium clusters Al_n ($n \leq 8$) as fragments of fcc lattice have been studied from an *ab initio* point of view. Complete geometry optimizations have been carried

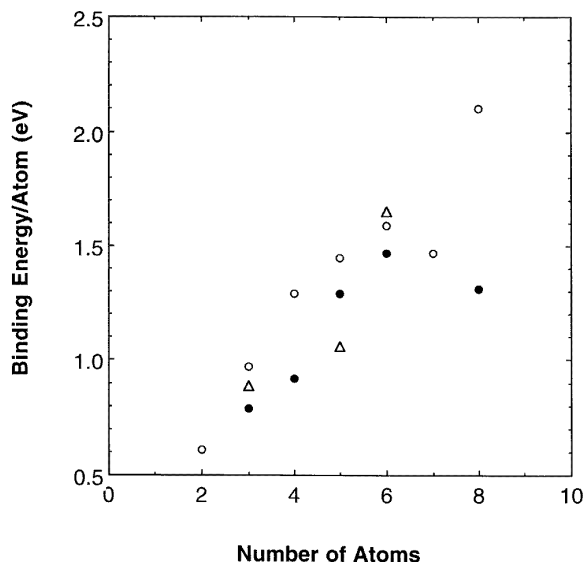


Figure 5. Binding energy per atom against number of atoms in different symmetries. The open circles, triangles, and filled circles represent the (100), (110), and (111) surfaces respectively.

out at the fourth-order many-body perturbation theory level. Possible clusters have been identified for future studies of chemisorption of different atoms/molecules on the aluminium surface. For the (100) surface Al_5 (4, 1) is a 'good' cluster, while for the (110) surface Al_5 (5, 0) appears to be a 'good' cluster. For the (111) surface, Al_8 (3, 3, 2) appears to be an ideal cluster for future studies of chemisorption.

Acknowledgments

The authors acknowledge partial support by the Department of Energy (DEFG05-87ER45316) for BKR and support from the Welch Foundation, Houston, TX (grant No Y-1092) for AKR. Computational support from the Pittsburgh National Science Foundation Supercomputing Center (grant No PHY930047P) and the University of Texas System Center for High Performance Computing are gratefully acknowledged.

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