Structure prediction of Al\textsubscript{n}O\textsubscript{m} clusters

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Abstract. Genetic algorithm simulations, using Buckingham potential to represent the anion-anion and cation-anion short-range interactions, were performed in order to predict the equilibrium positions of the Al and O ions in Al\textsubscript{n}O\textsubscript{m} clusters. In order to find the equilibrium structures of compounds a self-organizing genetic algorithm were constructed. The calculation were carried out for several clusters Al\textsubscript{n}O\textsubscript{m}, with different numbers of aluminium and oxygen atoms.

1. Introduction
Determining the global energy minimum of a molecule or a crystal is a serious problem. Depending on the goals and levels of investigation, the elementary object of consideration can be the overall of a crystal, a single molecule or an ensemble of molecules. The methods employed to determine the structure of the ground state and low energy of molecules can be categorized as either deterministic or stochastic. The deterministic methods, such as ab initio\cite{1} and DFT\cite{2} are generally considered to be most informative but are computationally expensive to implement, especially for large clusters or an ensemble of molecules. Semi empirical methods employs potentials with parameters adjusted to experimental data. Such potentials can often include effects beyond the scope of the formalism\cite{3}. Therefore results obtained by the means of these potentials are often used as a start point for DFT calculation. The stochastic methods such as Monte Carlo\cite{4} or molecular dynamics simulated annealing\cite{5,6} often encounter with difficulties\cite{7}. They require high accuracy in using force fields, a proper accounting for interactions, and considerable computer time.

Genetic algorithms, proposed by Holland\cite{8}, are global optimization method which are inspired by Darwinian natural evolution. A conventional genetic algorithm can be described in four steps. a) It uses an encoding of the control variables, called individuals; b) Genetic algorithm searches from one population of possible solutions to another population; c) It uses only objective function information (not derivatives); d) GA bases on probabilistic rules(not deterministic). It is an intelligent and information efficient approach\cite{9} to multi-variable, global optimization and has been successfully applied to a large number of complex problems\cite{10-16}.

Genetic algorithm developed and tested in this work starts from a randomly generated initial population. We use the Cartesian coordinates of the ions as a natural coding, and each cluster's fitness is computed based on its potential energy. After the fitness has been assigned to each cluster we change the position of each ion in the cluster. A new ion's position is accepted on condition that new cluster's fitness is better that the previous one. This procedure is repeated for many generations until the global minimum or at least a very good local minimum has been found.

In the following section of this paper we describe the above algorithm in detail. In section III the algorithm is applied to Al\textsubscript{n}O\textsubscript{m} clusters.
2. Method

The model of molecular problem consists of $N$ ions. The potential energy, $V$, of this system is given by the Buckingham potential:

$$V = \sum (q_i q_j / r_{ij}) + A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij} r_{ij}^{-6}$$ (1)

Where the summation over $i$ and $j$ includes unique pairs of ions, and $q_i$ is the charge of ion $i$, and $r_{ij}$ denotes the distance between ions $i$ and $j$. The first term represents the Coulomb interaction between an ion $i$ of charge $q_i$ and an ion $j$ of charge $q_j$ that are a distance $r_{ij}$ apart and the remaining terms constitute the Buckingham potential representing the anion-anion and cation-anion short-range interactions. Although alternative functions can be used for the latter, the Buckingham form has proved to be particularly effective. The potential parameters, $A_{ij}$, $\rho_{ij}$, and $C_{ij}$, may be derived using standard empirical fitting techniques[17,18]. The sets of parameters $A_{ij}$, $C_{ij}$, and $\rho_{ij}$ for each pair of ionic species are displayed in Table I.

| Interaction | $A_{ij}$ (eV) | $\rho$ (Å$^{-1}$) | $C_{ij}$ (eV Å$^{-1}$) |
|-------------|---------------|-------------------|------------------------|
| Al - Al     | 0.0           | 0.100             | 0.00                   |
| O - O       | 22764.0       | 0.149             | 27.88                  |
| Al - O      | 1460.3        | 0.299             | 0.00                   |

A flow chart representing the operation of our cluster geometry optimization program is shown in Fig. 1. A starting generation consisting of a certain number $N_{\text{pop}}$ (100 in our case) of clusters is generated. The Cartesian coordinates of each cluster ions are chosen randomly in a cubic box with length

$$L = (N \cdot \Omega)^{1/3}$$ (2)

where $N$ is the number of ions per cluster, and $\Omega$ (800 Å in our case) is the volume per ion. In our algorithm we use very simple crossover and mutation operators. The coordinates of each ion are changed independently by a little distortion:

$$X_{i,i+1} = X_{i,n} \cdot (1 + 0.5 \cdot \text{DIST} \cdot \text{RND}[-0.5;0.5])$$ (3)

Where $\text{DIST}$ is a distortion parameter (0.125 in our case), $\text{RND}[-0.5,0.5]$ [19] is a random number from the range of -0.5 to 0.5, and $i$ denotes $x$, $y$, $z$ coordinates. After a coordinate of the ion has been changed the potential energy (Eq. 1) is calculated for each cluster, and the new position of the ion is accepted only on condition that the potential energy of the new ions configuration is smaller than the old one, otherwise the previous position of the ion is restored. This procedure is repeated until a stable configuration has been found or there is no change of ions position of the cluster for more than 1000 generation.
To ensure that the whole space of consideration is taken into account we introduce a mutation operator. For each cluster we choose one ion for which a new position is generated randomly. The probability of the mutation we set to 0.0125, this step of the algorithm significantly slows the calculation. In order to control the process of forming the clusters we impose restrictions on the distance between ions and the positions of the ions. A minimal $r_{\text{min}}$ distance between two ions we set to 0.5 Å and 1.5 Å, whenever a distance between two ions is smaller than $r_{\text{min}}$, a new position of the ion is generated. The second restriction reduces the space allocated to the cluster, every time the position of the ion is outside of the cubic box a new position is generated.

3. Results and discussion

We now present the simulation results for several populations composed of clusters with different numbers of aluminium and oxygen atoms. The results show a huge number of different configurations and therefore we had to divide clusters into two groups. The first group consists of clusters that have at least one symmetry element whereas the second group holds clusters without symmetry elements. Below we consider only clusters from the first group.

In order to present our results in clearly form we grouped all clusters according to the number of aluminium atoms. The lowest energies we observe for Al$_3$O$_3$ (-3.66 eV) (fig. 2c), Al$_4$O$_6$ (-7.72 eV) (fig. 4d.), Al$_5$O$_6$ (-11.93 eV) (fig. 5e.) and Al$_7$O$_7$ (-14.42 eV) (fig. 6f.). Figure 3 shows that, in all four groups, the binding energy increases when the number of oxygen atoms reach the critical value. The main cause of this fact is the strong repulsive interaction between oxygen ions. This stops clusters growth and leads to the splitting of the forming clusters into small fraction what significantly disturb the positions of the ions inside the clusters. The origin of this distortion can be found in nonbonding interaction between separated clusters. For these cases we do not observe clusters with symmetry elements.
Further calculations showed simple solution of this problem. A strong repulsive interaction between oxygen ions can be reduced by forming \( \text{O}_2 \) groups (fig. 2c, fig. 4bcde, fig. 5ae, fig. 6abc) and \( \text{O}_3 \) groups. In some cases, especially for large number of atoms, \( \text{O}_3 \) groups take a shape of a line or an arc which are always composed into clusters. The energy binding of clusters containing \( \text{O}_3 \) groups are always higher than those with \( \text{O}_2 \) groups.

**Figure 2.** Low energy clusters \( \text{Al}_1 \text{O}_{m} \). The numbers under the structures are binding energies in eV.

**Figure 3.** Binding energies for \( \text{Al}_1 \text{O}_{m} \) clusters.
**Figure 4.** Low energy clusters $\text{Al}_2\text{O}_m$. The numbers under the structures are binding energies in eV.

**Figure 5.** Low energy clusters $\text{Al}_3\text{O}_m$. The numbers under the structures are binding energies in eV.
The calculations showed that the clusters grow can be controlled by the $r_{\text{min}}$ parameter. A small value (0.5 Å in our case) produces O$_2$ groups what leads to close clusters Fig. 4c, Fig. 4f, Fig. 5a, Fig. 5e, Fig. 6a, whereas a big value (1.5 Å in our case) produces loosely structured clusters Fig. 4e, Fig. 5b, 5c, 5d, 5f, Fig. 6d-f. Each O$^2-$ oxygen ion is surrounded either by 2 or 3, 4 and 5 Al$^{3+}$ ions. The average Al-O bondlength is 2.67 Å (fig. 7) and it is bigger than the Al-O distance observed in α-Al$_2$O$_3$[20,21]. The smallest (2.57 Å) Al-O distance we observe for AlO cluster whereas the highest value 2.98 Å we found for Al$_4$O$_2$. In contrary to Al-O the Al-Al distance distribution (fig. 7) has three peaks at 3.91 Å, 4.41 Å and 5.53 Å. The Al-Al distances are closely connected with the position of O$^2-$ oxygen ions in the clusters. The first peak at 3.91 Å can be assigned to clusters with O$^2-$ oxygen ions surrounded by three Al$^{3+}$ ions(Al$_2$O$_2$, Al$_3$O$_4$, Al$_5$O$_7$, Al$_2$O$_4$, Al$_4$O$_6$), the third peak can be assigned with clusters containing linear Al$_2$O or Al$_2$O$_2$ conformation and the last one with cluster containing disordered Al$_2$O$_2$ conformation or Al$_3$O$_3$ rings. In consequence we do not observe direct Al-Al bonds. 

Tree sharp peaks can be seen for O-O distance distribution. The first peak at 1.32 Å is connected with direct O-O bonds, whereas the second one at 3.94 Å is strongly connected with clusters composed of O$_2$ conformations and O$^2-$ oxygen ion(Al$_2$O$_3$, Al$_2$O$_6$, Al$_3$O$_6$). The last one at 5.13 Å can be assigned to cluster with Al$^{3+}$ ions surrounded by three O$^2-$ oxygen ions. We should noticed that the agreement between previous reported DFT and ab initio calculations[22-30] and our results is good. The difference in bondlength can be reduced by adjusting the ions charge.
4. Conclusions

The main aim of this paper was to report the method and describe the success of our approach in finding the equilibrium positions of Al and O ions in Al\textsubscript{n}O\textsubscript{m} clusters. We can control the process of forming Al\textsubscript{n}O\textsubscript{m} clusters either by the means of minimal distance between ions or the ions charges. Our algorithm is applicable to complicated chemical problems. There are no limits for number of ions or finite cluster. Comparison with DFT and ab initio results shows a convincing consistency with the cluster structures obtained in this work.

**Figure 7.** The distribution of interatomic Al-Al, Al-O and O-O distances.
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