

# Regional DFT - Electronic Stress Tensor Study of Aluminum Nanostructures for Hydrogen Storage

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**Abstract.** Nowadays, when technology has already been moved to the area of nano-devices, the description of properties at very microscopic level, within molecules, concerning interatomic interactions, had gained remarkable importance. Since these properties come to affect functionality and reliability of manufactured devices it is crucial to understand how to transfer practicality of macro-devices to nano (or subnano) level and what interferes with desirable features. The new materials for hydrogen storage devices might possibly be based on Al-nanostructures. We have modeled the structures and properties of Al-clusters and characterized atomic and molecular hydrogen adsorbed on its surface. The internal framework of clusters was studied using the Regional DFT method [1] and the insights into bond strengths and surface reactivity originating from the electronic stress tensor [2,3] has been given. The stress tensors are widely used to describe internal forces of matter. In molecules, the electronic stress tensor describes distortion of the charge density which has primary significance for physical and chemical properties being displayed by the system.

**Keywords:** energy density, chemical potential, bond order, metal clusters, hydrogen storage.

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## INTRODUCTION

It is anticipated that new materials can be based on closed shell metal clusters, which turned out to be extremely stable [4]. The metal clusters were successfully described by the jellium model [5-7], which indicates that a closed electronic shell leads to particular stability. Among light metals, the aluminium clusters attract significant attention, since Al<sub>7</sub> and Al<sub>13</sub> were identified to be particularly stable [8] with electronic configuration close to the closed-shell magic number predicted by the jellium model [7]. Numerous studies [9-14] indicate that Al<sub>7</sub> and Al<sub>13</sub> should be in the special interest, while showing enhanced binding energy. It is suggested that passivation through hydrogen or alkali metals donating one electron to Al<sub>13</sub> to complete the electron shell can lead to stable structures. The understanding of hydrogen interaction with such clusters may lead to development of novel hydrogen adsorbing materials.

The experimentalists have already managed to produce stable, closed electronic shell Al-clusters [15-23]. The Al<sub>13</sub> icosahedral cluster was found to be able to adsorb a

hydrogen without a potential barrier [24]. The authors tried to adsorb 20, 30 and 42 hydrogen atoms at Al<sub>13</sub> however optimized structures had imaginary frequencies thus could not be considered to be stable.

In this work the analysis of the bonding and electronic structure in context of hydrogen adsorption ability in clusters based on icosahedral Al<sub>13</sub>, namely Al<sub>12</sub>M<sup>Z</sup> (where M: Mg, Al, Si and Z = -1, 0, 1) are tackled using the Regional DFT and electronic stress tensor method.

## REGIONAL DFT METHOD

The theoretical method [25-28] utilized in this study allows one to assign energy density to any point in space according to associated electronic density. The obtained energy density might be decomposed into following energy densities: the kinetic energy density, the external potential energy density, and the interelectron potential energy density [1]. The details of the theory can be found elsewhere [1,29-34] and here we would like to only briefly review a part of it, directly related to this study. The non-positively defined kinetic energy density  $n_T(\vec{r})$  [29] plays a particular role in the theoretical method used in this study. The unique concept of electronic drop ( $R_D$ ) and electronic ( $R_A$ ) atmosphere regions, separated with interface surface ( $S$ ) is used to define shape of atoms and molecules [29]. In the  $R_D$  region, where kinetic energy density  $n_T(\vec{r}) > 0$ , the classical movement of electrons is granted, while in  $R_A$  ( $n_T(\vec{r}) < 0$ ) only quantum effects for electrons are possible and the  $S$  defines a turning point for an electron.

$$n_T(\vec{r}) = -\frac{\hbar^2}{4m} \sum_i^{occ} v_i [\psi_i^*(\vec{r}) \Delta \psi_i(\vec{r}) + \Delta \psi_i^*(\vec{r}) \psi_i(\vec{r})], \quad (1)$$

$$\begin{aligned} R_D : n_T(\vec{r}) &> 0, \\ R_A : n_T(\vec{r}) &< 0, \\ S : n_T(\vec{r}) &= 0. \end{aligned} \quad (2)$$

The electronic structure of system under study is characterized using electronic stress tensor  $\tau^{skl}(\vec{r})$  [29, 32-33], which describes the internal distortion of electronic density. The three eigenvalues of stress tensor and their eigenvectors determining principal axis can be used for geometrical visualization of bonding as well as quantitative evaluation of its properties and reactive regions in molecules [2-3,35]. The trace over the eigenvalues of stress produces energy density  $\varepsilon(\vec{r})$  in non-relativistic limit of the Rigged QED [34].

$$\tau^{skl}(\vec{r}) = \frac{\hbar^2}{4m} \sum_i^{occ} v_i \left[ \psi_i^*(\vec{r}) \frac{\partial^2 \psi_i(\vec{r})}{\partial x^k \partial x^l} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \frac{\partial \psi_i(\vec{r})}{\partial x^l} + \frac{\partial^2 \psi_i^*(\vec{r})}{\partial x^k \partial x^l} \psi_i(\vec{r}) - \frac{\partial \psi_i^*(\vec{r})}{\partial x^l} \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right], \quad (3)$$

$$\langle \hat{\tau}^S(\vec{r}) \rangle = \begin{bmatrix} \tau_{xx}^S(\vec{r}) & \tau_{xy}^S(\vec{r}) & \tau_{xz}^S(\vec{r}) \\ \tau_{yx}^S(\vec{r}) & \tau_{yy}^S(\vec{r}) & \tau_{yz}^S(\vec{r}) \\ \tau_{zx}^S(\vec{r}) & \tau_{zy}^S(\vec{r}) & \tau_{zz}^S(\vec{r}) \end{bmatrix} \xrightarrow{diag} \begin{bmatrix} \tau^{S11}(\vec{r}) & 0 & 0 \\ 0 & \tau^{S22}(\vec{r}) & 0 \\ 0 & 0 & \tau^{S33}(\vec{r}) \end{bmatrix}, \quad (4)$$

$$\tau^{S11}(\vec{r}) \leq \tau^{S22}(\vec{r}) \leq \tau^{S33}(\vec{r}), \quad (5)$$

$$\mathcal{E}(\vec{r}) = \frac{1}{2} \sum_k \tau^{Skk}(\vec{r}), \quad E = \int d^3\vec{r} \mathcal{E}(\vec{r}). \quad (6)$$

The total force acting on electrons in the system is composed of Lorentz force  $\hat{L}(\vec{r})$  and tension force  $\hat{\tau}^S(\vec{r})$ . For system in stationary state the total force at every point in space equals zero, thus Lorentz force exactly cancels the tension force.

$$\hat{F}(\vec{r}) = \hat{\tau}^S(\vec{r}) + \hat{L}(\vec{r}), \quad (7)$$

$$\langle \hat{\tau}^S(\vec{r}) \rangle + \langle \hat{L}(\vec{r}) \rangle = 0, \quad (8)$$

$$\hat{F}(\vec{r}) = \partial_i \tau^{skl}(\vec{r}) = \frac{\hbar^2}{4m} \sum_i^{occ} v_i \left[ \psi_i^*(\vec{r}) \frac{\partial \Delta \psi_i(\vec{r})}{\partial x^k} - \frac{\partial \psi_i^*(\vec{r})}{\partial x^k} \Delta \psi_i(\vec{r}) + \frac{\partial \Delta \psi_i^*(\vec{r})}{\partial x^k} \psi_i(\vec{r}) - \Delta \psi_i^*(\vec{r}) \frac{\partial \psi_i(\vec{r})}{\partial x^k} \right]. \quad (9)$$

If one investigate the tension force in the bonding regions of molecule in stationary state, one might find a point where (along with condition  $\hat{F}(\vec{r}) = 0$ ) the tension (as well as Lorentz force) itself will vanish and any force acting on electron density at that point will be zero [29,31,33-34]. The point is called a Lagrange point ( $\vec{r}_{Lagrange}$ ) and it is a stationary point for electron density distribution in a molecule [2-3]. The properties calculated at  $\vec{r}_{Lagrange}$  can be used to characterize respective interaction between atoms. The energy density based bond order indices were proposed [2-3]:

$$b_e = \frac{\mathcal{E}_{AB}(\vec{r}_{Lagrange})}{\mathcal{E}_{HH}(\vec{r}_{Lagrange})}, \quad (10)$$

$$b_{\mu} = \frac{\mathcal{E}_{AB}(\vec{r}_{Lagrange})}{n_{AB}(\vec{r}_{Lagrange})} \left( \frac{\mathcal{E}_{HH}(\vec{r}_{Lagrange})}{n_{HH}(\vec{r}_{Lagrange})} \right)^{-1}. \quad (11)$$

where  $\mathcal{E}_{AB}(\vec{r}_{Lagrange})$  is the energy density at the Lagrange point of bond of interest and  $\mathcal{E}_{HH}(\vec{r}_{Lagrange})$  is the energy density at Lagrange point of the H—H bond in a H<sub>2</sub> molecule. In  $b_{\mu}$  index,  $n_{AB}(\vec{r}_{Lagrange})$  and  $n_{HH}(\vec{r}_{Lagrange})$  denote corresponding electronic density respectively. The ratio of energy density to electronic density gives a linear approximation of the local electronic chemical potential  $\mu_R$  [2-3,35], thus  $b_{\mu}$  index is called chemical potential bond order.

$$\mu_R = \frac{\partial E}{\partial N} \approx \frac{\mathcal{E}(\vec{r})}{n(\vec{r})}. \quad (12)$$

## CALCULATION METHOD

The clusters were calculated using the exchange and gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBE) [36-37] and the one of Perdew and Wang (PW91) [38-39] with 6-31G(d,p) and 6-311G(d,p) basis sets in Gaussian 03 program package [40]. The respective electronic wavefunctions were used for the electronic stress tensor and energy density calculations in RDFT program package [41]. Visualizations of structures were done with VMD [42] and PyMol [43].

## RESULTS AND DISCUSSION

Since closed-shell clusters with the “magic” number of electrons were found to be particularly stable and Al<sub>13</sub> (a 39 valence electron system, one short for “magic” 40) may potentially be able to accommodate 20 or even 42 hydrogen atoms, we compared the electronic structures and properties of groups of clusters with modified central atom, which gave a set of structures with various electron count – from 37 to 41 electrons. We were specially interested in isoelectronic structures and the effect of the central atom on the cluster properties.

The effect of the exchange-correlation functional and basis set on calculated properties of studied clusters has been evaluated. No adverse effect of the exchange-correlation functionals used in calculations on cluster properties have been noticed. It was found that the double- $\zeta$  basis set results in lower bond order indices, lower electronic chemical potential on interface surface, lower electron density at terminal sites and higher electron density at hollow and bridge sites than the triple- $\zeta$  basis set. The double- $\zeta$  basis set results in more reasonable Mulliken atomic charges, which also correlate well with the electronic chemical potential redistribution in clusters.

The bond strengths measured with the energy density bond order ( $b_e$ ), of bonds between clusters atoms are about one order of magnitude lower than that of the H—H bond in a H<sub>2</sub> molecule. **Figure 1** shows dependence of bond strengths on interatomic

distance. The  $b_e$  index has linear dependence on bond length for different bond types and the total charge of cluster does not affect this trend. It was found that the bond strengths ( $b_e$  index, see **Fig.1** and **Tab.1**) of bonds between surface Al atoms and the central atom were generally higher than those between surface Al atoms. The Al—Si bonds (where Al was the atom on the cluster surface and Si - the atom at the cluster center) have higher strengths than Al—Al<sup>†</sup> (Al<sup>†</sup>: central atom), surface Al—Al or Al—Mg bonds with similar bond lengths. The average bond orders of surface Al—Al bonds were about 34%, 28% and 9% lower than indices associated with bonds involving central atom in clusters with Si, Al and Mg (as central atom) respectively. The corresponding differences were not dependent on the cluster charge or calculation method (**Tab.1**). The “magic” 40-electron systems are characterized by the highest average bond order indices.

The Al<sub>12</sub>Mg cluster has lower Al—Mg as well as Al—Al bond strengths than those in charged Al<sub>12</sub>Mg<sup>+1</sup> clusters, which might be related to the high spin density on the Mg atom in Al<sub>12</sub>Mg cluster (the Mulliken spin density is about twice the value of charged ones).

**Figure 2** compares clusters having different central atoms and total charge. The isoelectronic structures were placed in diagonal direction of the figure. Isoelectronic clusters display similar distribution of chemical potential on the surface. However the redistribution of chemical potential on cluster’s surfaces is very complex in general and will be discussed case by case in details. The 41-electron (total number of valence electrons) Al<sub>12</sub>Si<sup>-1</sup> cluster displays high local  $\mu$  on the whole surface, and only two Al atoms on opposite sides of cluster are characterized by higher local  $\mu$ . These Al atoms have weaker bonds with central Si atom as well as with neighboring surface Al atoms (similarly for the chemical potential bond order).

The 40-electron structures show very uniform and symmetric redistribution of chemical potential as well as  $b_e$  and  $b_\mu$  indices. The Al<sub>12</sub>Si shows lower  $\mu$  on the surface than isoelectronic, but negatively charged Al<sub>13</sub><sup>-1</sup>.

Next the 39-electron system possesses two low chemical potential hollow sites on opposite sides of the cluster; bond strengths of three Al atoms around the hollow site, with central atom, are greater than other surface Al atom – central atom connections. The mutual bonding between the three hollow site Al atoms is weaker than between those to other neighboring Al atoms (it applies also to the chemical potential bond order).

The 38-electron clusters show very uniform redistribution of chemical potential; the Al<sub>13</sub><sup>+1</sup> shows common features along with isoelectronic Al<sub>12</sub>Mg and the 37-electron Al<sub>12</sub>Mg<sup>+1</sup> cluster. There are few Al—Al bonds for which Lagrange points were not found (in Al<sub>13</sub><sup>+1</sup>, Al<sub>12</sub>Mg<sup>+1</sup>), the corresponding bond lengths were longer than 3Å, which is around 10% longer than average Al—Al bond distance in those clusters.

The chemical potential on the cluster surface increases from positively charged (lower  $\mu$ ) clusters to negatively charged (higher  $\mu$ ) ones (for the isoelectronic case as well as among structures with the same central atom). The chemical potential around core region of Si atoms is much lower than that of Al atoms, and Mg has the highest chemical potential around the core region; the electronic chemical potential around the core regions of Mg, Al and Si atoms correlate with their Mulliken atomic charges (see **Fig. 3**), where the Si atom has the lowest (negative) charge and the Mg atom the

highest (positive) charge, thus electrons tend to migrate in a cluster from regions of high  $\mu$  to regions of low  $\mu$ . The diameter of the core regions (which was assumed to be confined by the internal interface surface of the kinetic energy density closing the valence electrons region) of Mg, Al and Si atoms correlates with atomic radii of the elements.

## CONCLUSIONS

We have found that hydrogen adsorption on the Al-cluster surface is site-dependent. It was found for smaller tetrahedral Al<sub>4</sub> clusters (unpublished results) that at low chemical potential sites hydrogen adsorption goes without reaction barrier, while at high chemical potential sites there appears an activation barrier. The product of hydrogen adsorption at low chemical potential site may not necessarily be the most stable one. We suggest that also in larger clusters studied here, the activation barrier of adsorption should disappear (or be the smallest) at low chemical potential sites. Positively charged clusters display lower chemical potential at the surface thus should be more suitable for hydrogen adsorption than neutral or negatively charged species. The energy density bond orders show dissipation/partition of energy between bonds in molecules. Stronger bonds between central atom and surface Al atoms were observed for atoms in proximity of low- $\mu$  sites. The clusters containing a Si atom possessed higher energy density bond orders comparing to Al-only or Mg containing clusters. The positively charged Si-doped clusters are potentially improved, comparing to pure Al structures, basics blocks for hydrogen storage materials.

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