First Principles Investigation on \( H_2 \) Adsorption on the Pristine 2-Dimensional Hexagonal Aluminum

A R Villagracia\textsuperscript{1,3*}, H L Ong\textsuperscript{2}, M David\textsuperscript{1,3} and N Arboleda Jr\textsuperscript{1,3}

1 Physics Department, De La Salle University, Manila, Philippines 0922
2 School of Materials Engineering, Universiti Malaysia Perlis, Arau, Perlis, Malaysia
3 Advanced Nanomaterials Investigation by Molecular Simulations, DLSU, Manila

E-mail: arcvillagracia@gmail.com

Abstract. Lightweight hydrogen storage with high storage capacity is one of the challenges in pursuing a hydrogen economy as a source of clean energy. Aluminum has been proposed as a material for storage and production of hydrogen. Recent theoretical studies have established the feasibility of 2D hexagonal lattice structure aluminum. In this study theoretical investigation on 2D h-aluminum was performed employing density functional theory to study the energetics of hydrogen molecule and 2D h-aluminum system. Hydrogen molecule on top, hollow and bridge sites of hexagonal lattice were geometrically optimized to determine if hydrogen molecule would dissociate or adsorbed as a molecule. Results showed that hydrogen molecule can be physisorped mainly in the bridge site (\(-0.463\) eV) at a distance of 3.1 Å, while it can dissociate at the top site with an activation energy of 1.51 eV. Electron density difference shows transfer of 0.60\(e^-\) from hydrogen atoms to the aluminum atoms. Density of states showed broadening of energy levels and their general shift towards lower energies, and alignment of the orbitals showing sp hybridization. Results of this study can be used in further investigation on doped or decorated systems of 2D h-aluminum.

1. Introduction
With the increasing number of world population comes with increasing demand for clean energy [1]. Several efforts of the government, industry and scientific community to find ways in generating electricity using clean energy, and avoiding CO\(_2\) emission from the number one source of energy: coal [2]. Hydrogen fuel cell is found to be one of the possible sources of clean energy with water as the only product of the reaction. With hydrogen (H\(_2\)) and oxygen (O\(_2\)) gas as its input, storing hydrogen gas would be one of its hurdles due to its low density that can be used for transportation [3]. Currently, hydrogen gas are stored by cryo-compression, liquefied, or adsorbed/absorbed on metals or chemical compounds [4-7]. However, high amount of energy is normally needed to store it for the first three methods, while additional reactions and/or chemicals are needed to extract the hydrogen gas. Further studies are being researched for chemically stored hydrogen gas. An example of this studies is the extraction and storage of hydrogen molecules on metal hydrides such as aluminum, gallium, indium and tin via exothermic reaction [8-9].
Among these metals, bulk aluminum has been found to produce hydrogen and aluminum hydroxide via water splitting. This can be recycled back to aluminum via Hall-Heroult process [10-12]. However, this would not be practical for long term storage and/or application for transportation.

Recently, a two-dimensional aluminum has been studied computationally, and verified its stability using density functional theory [13-15]. Different stable structures of 2D-aluminum were found to be stable. One of them is hexagonal honeycomb structure which is called aluminene. This recent study leads to a possible storage material for hydrogen gas.

In this study, hydrogen adsorption on a pure 2-D hexagonal aluminum was investigated using the novel density functional theory. Numerous studies on hydrogen storage uses density functional theory to study the adsorption of atoms on different surfaces [16-22]. As of today, no other study has been found on planar aluminene monolayer as a hydrogen storage material.

2. Methodology
Density functional theory [23] is employed to optimize the geometric structure of aluminene, and calculated its ground state properties such as energy, density of states, charge density and band structures. The unit cell of aluminene is composed of two aluminum atoms with a symmetry of P6/mmm spacegroup as shown in figure 1a. A vacuum of 20 Å along the z-axis has been set to simulate a single plane of aluminene, and to avoid self-interaction of aluminene images. The geometric structure of hydrogen molecule was optimized, and its ground state properties were also calculated.

![Figure 1.](image_url)

**Figure 1.** (a) hexagonal lattice of aluminene (b) \( \text{H}_2 \) adsorption sites and \( \text{H}_2 \) orientation (c) Super cell

After geometry optimization of a unit cell, a 3x3 super cell was generated for hydrogen adsorption as shown in Figure 1b. Three adsorption sites (top, hollow, bridge) were identified and two orientations (parallel to x-axis: A, parallel to y-axis: B) of hydrogen molecule were used in this study. The center of mass of the hydrogen molecule was used as the reference for their initial positions. Total energy calculations of the static system (hydrogen on aluminene) were performed. The hydrogen molecule approaches the aluminene from 1 Å to 5 Å perpendicular to the surface with an increment of 0.4 Å as shown in Figure 1c. The purpose of these calculations is to check for immediate adsorption on the sites without relaxation.

Relaxed structural calculations of the systems (all atoms are allowed to move) were performed where \( \text{H}_2 \) is above the surface by 1 Å, and systems with the lowest energy position based on the calculations result on static system. The resulting structures either yielded a dissociated \( \text{H}_2 \) molecule and non-dissociated \( \text{H}_2 \) molecule on aluminene surface. The optimized structures from the previous calculations were used as the initial (from optimized structure with \( \text{H}_2 @ \) lowest energy) and final image (from optimized structure with \( \text{H}_2 @ \) 1 Å) for the nudged elastic band calculation on system where \( \text{H}_2 \) molecule dissociated and absorbed to the aluminene surface. This provided a more accurate dissociation energy barrier.
2.1 Calculation Details
Quantum Espresso [24] was used to perform the DFT calculations. The exchange-correlation (XC) potential used in this study is the generalized gradient approximation Perdew–Burke–Ernzerhof (PBE) [25]. The Rappe–Rabe–Kaxiras–Joannopoulos (RRJK) ultrasoft pseudopotential [26] with scalar-relativistic effect for aluminum atom was used. The kinetic energy cutoff set was 50 Ry for electronic wave functions. A $51 \times 51 \times 1$ Monkhorst–Pack k-point sampling of the Brillouin zone integrations, $10^{10}$ Rydberg convergence criteria for the energy self-consistent calculations, and $10^{-3}$ Ry/Bohr for force convergence criteria were used in the calculations. The total energy of isolated $H_2$ molecule, $3\times3$ unit cell of aluminene, and the combined systems were calculated. The energy difference of the combined systems with sum of the isolated $H_2$ molecule and pristine aluminene were calculated as shown in equation 1

$$E_{\text{diff}} = E_{\text{combined}} - (E_{H_2} + E_{3\times3\ Al})$$

3. Results and Discussion
3.1 Band Structure and Static System Results

The optimized structure of the planar 2D aluminene is shown in Figure 1. It has a lattice constant of 4.4891 Å and the calculated formation energy is -2.91 eV. These results agree with the results of previous studies. No buckling height was obtained during the geometry optimization. The band structure (Figure 2a) were also compared to the previous studies [13-15] as shown in Figure 2. The band structure resembles the band structure of 2D materials which has a distinct Dirac-cones. Figure 2b shows the energy difference calculations for static systems of $H_2$ molecule as it approaches the perpendicular to the aluminene surface. Unlike in bridge and top sites, the energy differences calculated at the hollow site is the same regardless of the orientation of the $H_2$ molecule. All sites are possible binding sites at all orientation around 3.0 Å to 3.6 Å with the bridge site parallel to y-axis having the most negative adsorption energy of -0.44 eV, while the other sites having a negligible binding energy from -0.05 eV to -0.01 eV.

3.2. Relaxed System and Nudged Elastic Band Calculation
A total of twelve (12) systems from the six (6) system configurations were optimized in which all atoms are allowed to move. Table 1 summarizes the results of the relaxed systems with and without dispersion correction. The hydrogen molecule did not dissociate after optimization when it was near or far from the surface on bridge and hollow sites. At the top site near the surface, the $H_2$ molecule dissociates and moved separately into the bridge sites. This agrees with the results in the previous studies for clustered aluminum atoms [27-29]. However, the $H_2$ molecule did not dissociate when it is far from the surface. This means that there is an energy barrier in order for the $H_2$ molecule to dissociate.
Table 1. Energetics of Relaxed H\textsubscript{2} molecule on Aluminene Surface

| Position/Orientation | Dissociated | Z-Distance of H atoms (Å) | Adsorption Energy (eV) | with Dispersion Correction (eV) |
|----------------------|-------------|---------------------------|------------------------|-------------------------------|
| Top/Parallel to X    | Yes         | 1.191                     | -0.527                 | -0.606                        |
| Top/Parallel to X    | No          | 2.723 / 2.832             | -0.060                 | -0.093                        |
| Top/Parallel to Y    | No          | 2.264                     | 0.019                  | -0.034                        |
| Bridge/Parallel to X | No          | 3.287                     | -0.069                 | -0.111                        |
| Bridge/Parallel to Y | No          | 3.067                     | -0.463                 | -0.514                        |
| Hollow/Parallel to X | No          | 3.269                     | -0.072                 | -0.126                        |
| Hollow/Parallel to Y | No          | 3.307                     | -0.085                 | -0.122                        |

Figure 3. Reaction Path from NEB

In order to determine the energy barrier, a nudged-elastic band (NEB) calculation was performed implementing quasi-Newton Broyden's second method using 100 images. The initial image used here is the relaxed H\textsubscript{2} molecule on aluminene surface, and the dissociated H\textsubscript{2} molecule as the final image. Figure 3 shows the energy-path coordinate graph from the NEB calculation, and 10-image static calculation. The energy barrier is approximately 1.51 eV with a binding energy of -0.527 eV without dispersion correction, and -0.606 eV with energy dispersion correction. The transition state is when H\textsubscript{2} molecule is at a Z-distance of 1.441 Å, and H-H distance of 1.123 Å.

Figure 4. (a) Density of States Aluminum atom and H\textsubscript{2} Molecule; (b) electron density difference (slice): red (+), blue (-); (c) Mulliken population analysis

It can be seen in the density of states how the overlapping of s and p orbitals occurred as shown in Figure 4. The s-orbital of the hydrogen atoms spread out, while the s and p orbitals of nearby aluminum atoms shifted to the left and realigned with the s-orbital of hydrogen atoms. Using Mulliken population analysis, the aluminum atoms near the hydrogen atoms are more slightly positive,
while the hydrogen atoms are slightly negative indicating a charge transfer of 0.60e⁻. This creates an attraction between the hydrogen atoms and the surface. These results indicate aluminene as a good candidate as a hydrogen storage material with physisorption and chemisorption capability.

4. Conclusion
Adsorption of hydrogen molecule on hexagonal 2D-aluminum has been investigated using density functional theory. The bridge site has been found as the most stable adsorption site for hydrogen molecule without any energy barrier. On the other hand, hydrogen molecule can be dissociated with a 1.51 eV energy barrier. The hydrogen atoms are adsorbed in the bridge site. The desorption energy needed to release the hydrogen atoms is 2.37 eV. Further investigation are on-going for the maximum capacity of pristine 2D aluminum, and doped hexagonal 2D aluminum systems that may increase further the viability of its capacity as a hydrogen storage material.

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