D-band Center Theory for the Case of Hydrogen Atom Adsorption on Fe(100) and Al(100) Surfaces: A Density Functional Study

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Abstract. The adsorption process occurs in technology that involves the surface. This study aims at investigating the adsorption of hydrogen atom on iron (Fe) and aluminium (Al) surfaces by using d-band center theory based-on density functional theory (DFT) method. DBC theory has proven very useful to understand the formation bond and the tendency of reactivity of transition metal which can learn by electronic structure system. This study obtained electronic structure system which is described by projected density of states (PDOS) using a system that consist of hydrogen atom adsorbed on Fe and Al surfaces. The result of PDOS used to explain the results of adsorption energy. The antibonding states on Fe surface were unfilled, meanwhile on Al surface were filled. Those results was suitable with the adsorption energy calculation results which showed that the bond between hydrogen and Fe surface was stronger than the bond between hydrogen and Al surface.

Keywords: Fe(100) surface, Al(100) surface, Adsorption energy, d-band center theory, DFT

1. Introduction

Adsorption is involved in almost all technological processes involving surface [1]. Adsorption occurs when an atom or molecule binds to a surface. The atom or molecule that binds to the surface is called an adsorbate. In the adsorption process, a bond is formed between the surface atom and the adsorbate.

One of the theory that explains adsorption is the d-band center (DBC) theory [2]. DBC theory based on molecular orbital theory. The DBC theory explains the interactions between atom or molecule and surface based on adsorbate orbitals and d-orbitals of atoms on the surface. According to the d-band center theory, the adsorbate that binds to the surface can form energy bands.

The theory of d-band center was proposed by Hammer and Norskov to explain the adsorption of hydrogen atom on the surface of Nickel (Ni), Copper (Cu), Platinum (Pt) and Gold (Au) [2]. They reviewed the Projected Density of States (PDOS) system consisting of hydrogen adsorbed on the surface of Ni, Cu, Pt, and Au to determine hydrogen adsorption energy on the surface. They concluded that the adsorption energy is determined by the antibonding state and the orbital overlap integrals of the atoms that interact.

The purpose of this study is calculate the adsorption of hydrogen atoms on the surface of Fe and Al with the DBC theory. Hydrogen atom and transition metal surfaces interaction is fundamental in heterogeneous catalyst. Meanwhile, Fe and Al surface was chosen because it catalyze various hydrogenation reactions [3-6].

2. Computational Details

In this study we use Fe(100) and Al(100) as a surface model, with the vacuum space of 15 Å. There are 3 adsorption site models of hydrogen namely: top (T), bridge (B) and hollow (H). Figure 1 and 2 show the sites of hydrogen on Fe(100) and Al(100) surfaces, respectively. All calculations are implemented in opEn Source Package for Research in Electronic Structure, Simulation and Optimization (Quantum Espresso) [7]. The projected augmented wave (PAW) pseudopotential method is employed in order to describe the interaction between nuclei and electrons. The electron exchange correlation is treated using generalized gradient approximation (GGA) based on Perdew, Burke, and Ernzerhof (PBE) functional [8]. Monkhorst–Pack method [9] is used to sample k-points by using $8 \times 8 \times 1$ grid. Planewave basis set with a cut-off energy of 500 eV and Gaussian electron smearing method with $\sigma = 0.10$ eV are set. Geometry optimization are performed until the forces are less than 0.02 eV Å^{-1}. Energy threshold-defining self-consistency of the electron density is implemented at 10^{-6} eV.
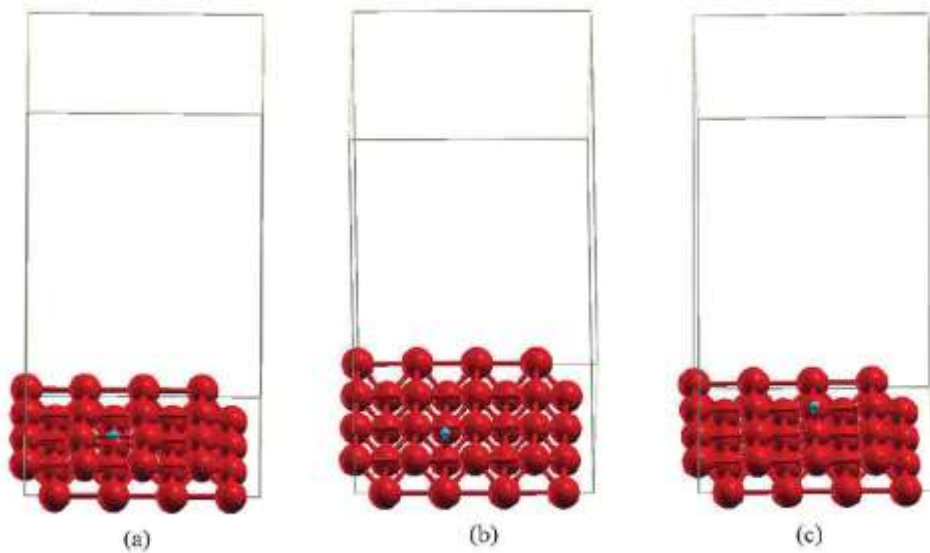

Figure 1. Adsorption site of hydrogen on Fe(100) surface. (a) bridge, (b) hollow, (c) top
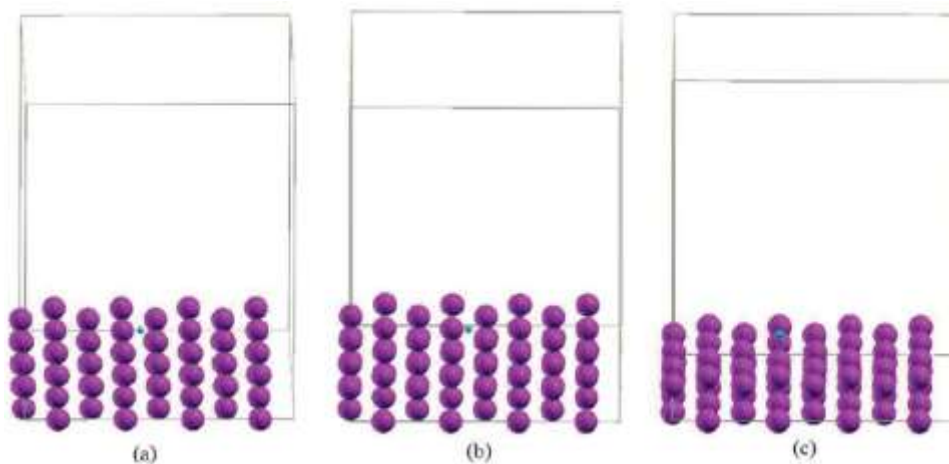

Figure 2. Adsorption site of hydrogen on Al(100) surface. (a) bridge, (b) hollow, (c) top

3. Results and Discussion

3.1. *Adsorption Energy*

Adsorption energies are computed by taking energy difference between optimized adsorption, optimized adsorbate in the gas phase and optimized surface according to:

$$E_{ads} = E_{(adsorbate\text{-}substrate)} - (E_{adsorbate} + E_{substrate}) \qquad (1)$$

where E_{ads} is the adsorption energy, $E_{(adsorbate\text{-}substrate)}$ is the total energy of adsorption, $E_{adsorbate}$ is the total energy of hydrogen atom, and $E_{substrate}$ is the total energy of surface. Negative value of adsorption energy indicates exothermic adsorption whereas positive value of adsorption energy indicates endothermic adsorption.
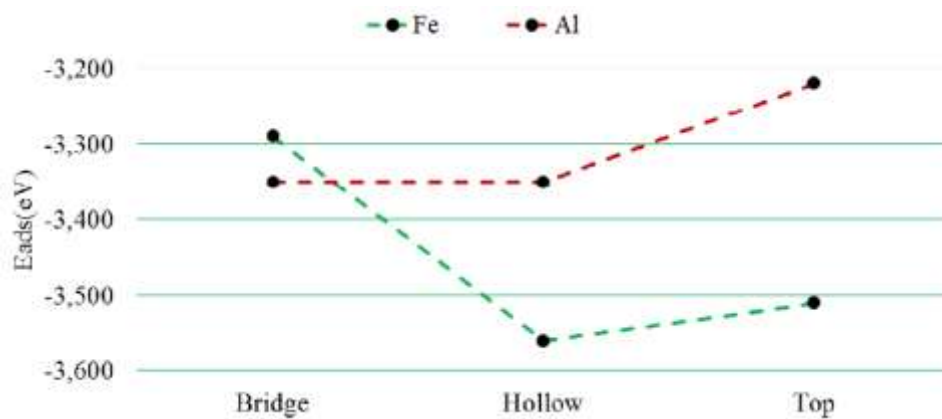

Figure 3. The comparison of hydrogen adsorption energy on Fe(100) and Al(100) surfaces.

Figure 3 shows the comparison of adsorption energy of hydrogen on Fe(100) and Al(100) surfaces. The adsorption energy on Fe(100) surface at bridge (B) site is -3.29 eV, while that at hollow (H) site and top (T) site are -3.56 eV and -3.51 eV, respectively. The adsorption energy on Al(100) surface at bridge (B) site, hollow (H) site and top (T) site are -3.35 eV; -3.36 eV and -3.22 eV, respectively. The stable configuration of hydrogen adsorption on Fe(100) surface and Al(100) surface are on the same site (hollow site). This indicates that at hollow site, the hydrogen atoms strongly bonded to the surface. Meanwhile, the comparison of hydrogen atom at hollow site on Fe(100) surface and Al(100) surface shows that hydrogen atom prefer to adsorp on Fe(100) surface than Al(100) surface.

3.2. *Projected Density of States (PDOS) of Systems*

Figure 4 shows the PDOS of *d*-orbital of Fe atom at the time when before adsorption and after adsorption at site B, site H, and site T. Whereas Figure 5 shows the PDOS of *s*-orbital of hydrogen atom at the time when before adsorption and after adsorption. The PDOS of Fe atom and H atom when before adsorption are almost same for all sites. This is because there is no interaction between the surface and hydrogen atom. After hydrogen adsorption on the surface, PDOS of *d*-orbital of Fe atom at B, H and T sites show that the antibonding state is unfilled. After the adsorption, the PDOS of *s*-orbital of hydrogen atom at H site shows the bonding state which is larger energy gap to Fermi level when compared to B site and T site. This causes the hydrogen atomic bond at H site is stronger than B and T sites. This is suitable with the adsorption energy calculation.
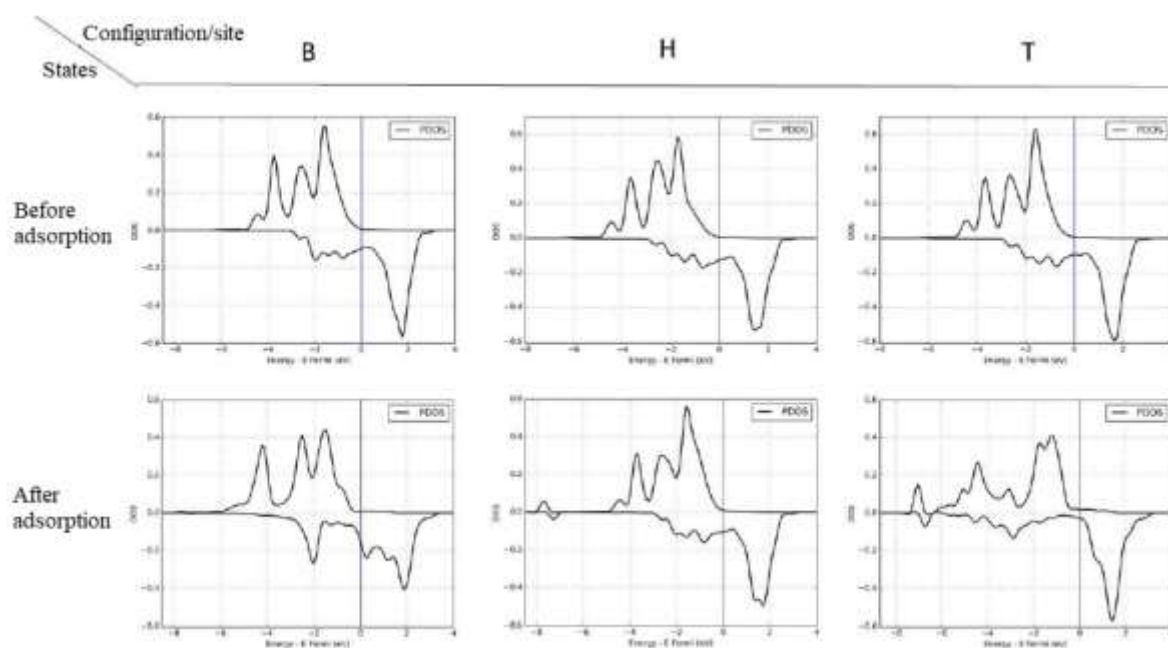
Figure 4. Projected density of states (PDOS) of *d*-orbital of Fe atom on Fe(100) surface at B, H and T site. (above) Before adsorption and (below) after adsorption.
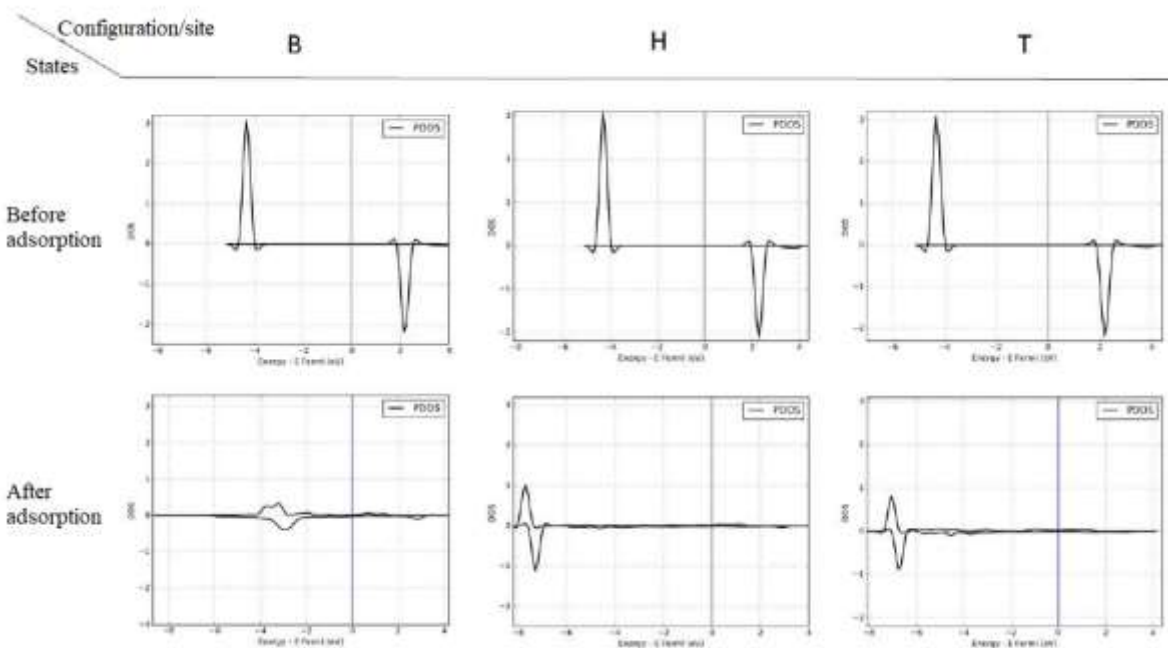

Figure 5. Projected density of states (PDOS) of *s*-orbital of H atom. (above) Before adsorption (isolated atom) and (below) after adsorption on Fe(100) surface.
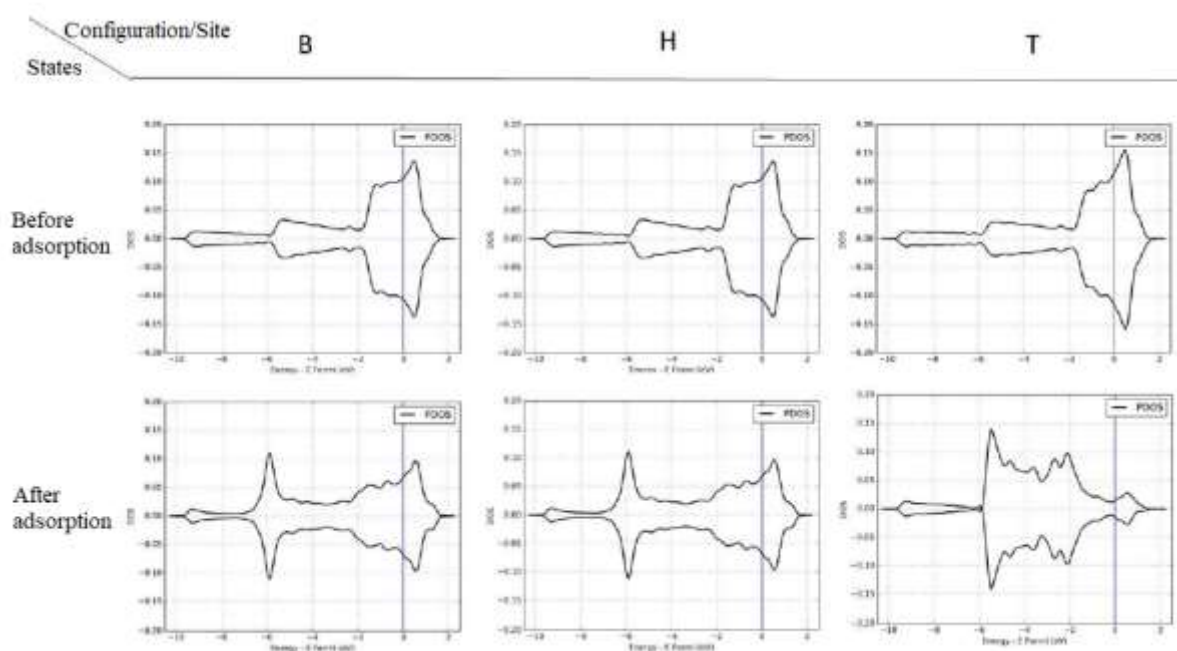
Figure 6. Projected density of states (PDOS) of *p*-orbital of Al atom on Al(100) surface at B, H and T site. (above) Before adsorption and (below) after adsorption.
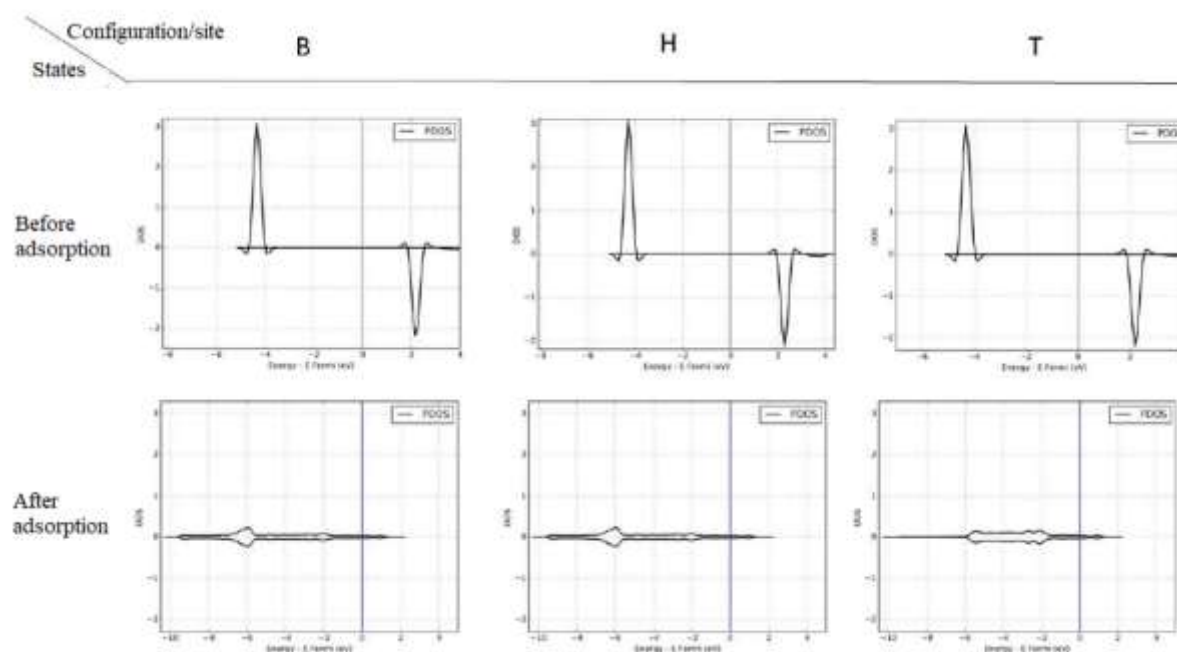

Figure 7. Projected density of states (PDOS) of *s*-orbital of H atom. (above) Before adsorption (isolated atom) and (below) after adsorption on Al(100) surface.

Figure 6 shows the PDOS of *p*-orbital of Al atom at the time when before adsorption and after adsorption at site B, site H, and site T. Whereas Figure 7 shows the PDOS of *s*-orbital of hydrogen atom at the time when before adsorption and after adsorption. The PDOS of Al atom and H atom when before adsorption are almost same for all sites. This is because there is no interaction between the surface and hydrogen atom. After hydrogen adsorption on the surface, PDOS of *p*-orbital of Al atom at T site has a bonding state which is smaller energy gap to Fermi level compared to B and H sites. Whereas the bonding state at B and H sites has almost the same energy gap to Fermi level. After the adsorption, the PDOS of *s*-orbital of hydrogen atom at T site shows the bonding state which is smaller energy gap to Fermi level when compared to B site and T site. This causes the hydrogen atomic bond at B and H sites is stronger than T sites. This is suitable with the adsorption energy calculation.

4.   Conclusion

Hydrogen (H) adsorption on Fe(100) and Al(100) surfaces has been investigated by using d-band center theory based on first-principles DFT method. The results of this study indicate that the position of the d-band center, antibonding and bonding state affect the adsorption of hydrogen atoms on the surface of Fe(100) and Al(100). Determination of antibonding and bonding states is done by projected density of states (PDOS) plots from the system. The results of this study show that on the surface of Fe(100), the strongest adsorption energy is at hollow (H) site, while the weakest adsorption energy is at bridge (B) site. This is indicated by the bonding state at H site has larger energy gap to the Fermi level compared to B site and T site. Meanwhile the bonding state at B site has smaller energy gap to the Fermi level compared to H site and T site. The adsorption energy of hydrogen on Al(100) surface show that H site is strongest adsorption energy. This is indicated by the bonding state at H site and B site has larger energy gap to Fermi level. Meanwhile at T site, the bonding state has smaller energy gap to the Fermi level compared to B site and H site. The adsorption energy on Fe(100) surface is stronger than on Al(100) surface. Hydrogen atom prefer to adsorp on Fe(100) surface. This is indicated by the antibonding state which is only filled on Al(100) surface. The results of this study indicate that the DBC theory can be used to explain the bonding of hydrogen atom to Fe(100) and Al(100) surfaces.

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