ORIGINALE ARTICLE

DENSITY FUNCTIONAL THEORY INVESTIGATION OF THE MOLECULAR AND DISSOCIATIVE ADSORPTION OF HYDROGEN ON PLATINUM SURFACES

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ABSTRACT

Background: The use of catalysts such as platinum is a common occurrence in industries involving chemical reactions. In the petrochemical industry, the transformation of hydrocarbons is always accompanied by hydrogenation and dehydrogenation reactions. These reactions always start with the adsorption of hydrogen on the surface of the catalyst. **Objectives**: The theoretical study of the phenomenon of hydrogen adsorption on a Pt (100) surface is the main aim of this work. **Methods**: The computation is performed using the density functional theory (DFT). The program DACAPO (Danish ab initio pseudopotential code) developed from the DFT based on the plane waves and pseudopotentials is used for all simulations. The adsorption energy and the interatomic distances are the principal calculated properties. **Results**: A study of the adsorption of the H2 molecule was carried out for various configurations which are distinguished by the sites where the molecule is placed and by the orientation of this molecule compared to surface. When direction H-H is perpendicular to the plane of surface, a weak interaction is established between the molecule and the surface. When direction H-H is parallel to the surface plane the interaction is stronger than what is obtained for the perpendicular direction to the surface plane. A study of the dissociate adsorption of hydrogen is also carried out. The calculations showed that the adsorption energy of the hydrogen atom on the surface depends on the location of the adsorption site. **Conclusions**: the study showed that the interaction of the molecule with the surface depends as well on the orientation of the molecule in relation to the surface than the type of site where this molecule is placed. From our calculations, it is clearly shown that the bridge sites are the most stable while the hollow sites are the least stable. A reduction in the energy of adsorption was noted when the deposit rate increases.
Keywords: *Catalysis; Platinum; Hydrogen; Danish ab initio pseudopotential code; Density Functional Theory.*

1. INTRODUCTION

Since its introduction in 1836 by Berzelius, catalysis has evolved into a well-established scientific field, thanks to the groundbreaking contributions of researchers such as Döbereiner, Ostwald, and Langmuir [1]. Catalysis is now recognized as the process of accelerating a chemical reaction through the use of a catalyst, a substance that remains unchanged and is not consumed during the reaction. This concept was first explored by Johann Wolfgang Döbereiner, a German chemist, who observed that certain substances could enhance the rate of chemical reactions without being consumed in the process [2].

Heterogeneous catalysis plays a vital industrial role, where gaseous reactants interact with solid catalysts. For example, petrochemical and pharmaceutical production rely heavily on heterogeneous catalysts. Enzymes provide examples of homogeneous catalysts that regulate biological functions. Pollution from industrial activities generates unwanted byproducts, yet heterogeneous catalysis effectively decomposes many such waste compounds. The initial step in heterogeneous catalysis involves adsorption of reactants onto catalyst surfaces. Two adsorption modes exist - physical (physisorption) through weak van der Waals interactions, and stronger chemical (chemisorption) bonding.

Automobile exhaust presents pollution challenges through emission of nitrogen oxides (NO_x) and carbon monoxide (CO). Controlling these gases is critical due their environmental and health impacts. Catalytic reduction of NO_x by hydrocarbons or hydrogen provides effective emission abatement strategies. Platinum is a widely applied heterogeneous catalyst, but research into alternative metals continues. Understanding hydrogen adsorption represents a fundamental first step towards elucidating reactions involving this small molecule. Specifically, this work focuses on the hydrogen-platinum (100) surface interaction as a model system. Density functional theory calculations will be performed to investigate the molecular and dissociative adsorption configurations and energetics of hydrogen on the Pt (100) surface. Insights from this theoretical study aim to further develop structure-function relationships in heterogeneous catalysis and pollution control.

2. MATERIALS AND METHODS

2.1 Computational method

In this work, we utilized the Dacapo program developed by the Center for Atomic-scale Materials Physics (CAMP) at the Technical University of Denmark [3, 4]. This code is based on the density functional theory (DFT). The valence electron-ion interactions are simulated by using pseudopotentials developed by Vanderbilt [5]. Functional (GGA) parameterized

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by Perdew-Wang (PW91) was used for the exchange-correlation part [6, 7]. All forces are calculated by using the Hellmann-Feynman theorem [8] and geometry optimization was conducted by using the BFGS method. Brillouin zone sampling utilized generation of k-points using the Monkhorst and Pack method [9]. In our calculations, the force gradient threshold must be less than or equal to 0.05eV/Å.

To achieve good accuracy in calculations, a sufficiently high density of k-points is required, but increasing the density of k-points also extends the computation time. Moussounda et al., (2007) [10] estimated that a k-point density of (5x5x1) is adequate for the (2x2) Pt(100) cell, and we have therefore maintained this density (5x5x1). For the cutoff energy, Baraldi et al., (2004) [11] demonstrated that a value of 340eV is sufficient for transition metals. We have considered a cutoff energy of 350eV for all our calculations.

2.2 Parameters related to the supercell

The DACAPO code requires the system to be translationally invariant for the applicability of the Bloch theorem. However, for a surface, translational invariance is not maintained along the axis normal to the surface plane. Additionally, it is reasonable to assume that only a certain number of layers starting from the surface influence the adsorbed atoms on the surface. We can then replace the real system with the repetition of a supercell (see figure 1) that contains a certain number of metallic planes (slabs) and empty space. The system becomes periodic through translation in all three directions.

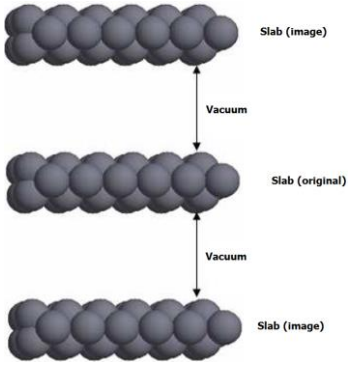

Figure 1: The figure shows the principle of supercell.

The thickness of the slab and the size of the vacuum space are crucial criteria for the calculations. The greater the number of layers considered, the more precision can be achieved, but computation time increases. Therefore, we considered a slab with three layers. We will compare our results with findings from other studies that used four and five layers. The vacuum space we utilized corresponds to approximately 20Å, where Moussounda (2006) [12] estimated that around 18Å of vacuum space is needed for the interactions between successive slabs to become negligible.

2.3 Construction of the surface

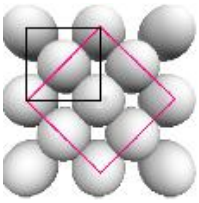

Figure 2: The figure represents a surface (2x2) (pink square), and a surface $(\sqrt{2} \times \sqrt{2})R45$ (black square).

We utilized a (2x2) unit cell of a (100) plane of Pt. Choosing a (2x2) unit cell allows for studies covering a broader range of coverage ratios compared to using a (1x1) unit cell. Figure 2 provides a clear visualization of this (2x2) Pt (100) unit cell.

2.4 Adsorption of H_2 molecule

When studying the adsorption of a molecule on a surface, three key points are of particular interest:

- The geometry of the adsorbed molecule will be compared to that of the isolated molecule in the gas phase.
- The adsorption energy of the molecule will be evaluated to investigate the stability of the {molecule+substrate} system.
- Comparisons of the Local Density of States (LDOS) of different atoms in the {molecule+substrate} system with the LDOS of the atoms in the isolated molecule and the atoms on the clean surface will be performed.

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By convention, the adsorption energy of the molecule is defined as:

$$E_{adsorption} = E_{system} - [E_{slab} - E_{molecule}] \quad (1)$$

Where:
E_{system} represents the total energy of the {molecule+slab} system,
$E_{molecule}$ is the total energy of the molecule in the gas phase,
E_{slab} is the total energy of the isolated slab (substrate).

Note that $E_{adsorption} < 0$ corresponds to stability of the {molecule+substrate} whole system, and the system is more stable when the absolute value of $E_{adsorption}$ is larger.
E_{slab} is calculated by relaxing the surface atoms of platinum, while E_{system} is calculated by simultaneously relaxing the molecule and the surface plane, minimizing the total energy until convergence is reached. These energies are calculated with the same k-points and the same cutoff energy.
The adsorption of H_2 has been studied on three high-symmetry sites of the (2x2) surface of Pt(100) (see figure 3).

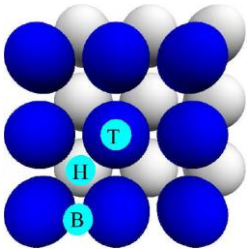

Figure 3: The figure presents the 3 sites absorption: T (aTop or apical), B (Bridge), H (Hollow). Blue spheres are platinum on surface and grays spheres are platinum at subsurface.

Various orientations of the H_2 molecule were examined on the three sites, depending on whether only one H atom is in contact with the surface plane or two H atoms are in contact with the surface plane.
To simplify notations, each configuration is denoted by the site label (T, B, or H) followed by the number of H atoms (1 or 2) in contact with the surface plane.

2.5 Adsorption of H atoms

The study of the adsorption of the hydrogen atom on a metal surface is an important part in the study of the adsorption of the H_2 molecule on a surface. This study could make it possible to predict the stable configurations for the adsorption of H in the event that the H_2 molecule were to dissociate or in more general cases where a molecule containing an H atom released this hydrogen atom after dissociation of the molecule. We studied hydrogen adsorption (dissociative adsorption) for several configurations and for different coverage rates. The coverage rate is defined as the ratio of the number of H atoms adsorbed on a cell and the number of Pt atoms, on the surface, contained in this same cell. To vary this coverage rate, we can change the size of the cell or vary the number of H atoms in a cell.

For a (2x2) cell, the coverage rate is 1 when we adsorb 4 H atoms in this cell. For the cell $(\sqrt{2} \times \sqrt{2})R45$ the coverage rate is 1 when 2 H atoms are placed in this cell.

For these different coverage rates, the adsorption energy ($E_{adsorption}$) of hydrogen is calculated from the formula:

$$E_{adsorption} = \frac{\left[E_{nH/Pt} - \left(E_{Pt} + \frac{n}{2}E_{H_2}\right)\right]}{n} \quad (2)$$

Where:
$E_{nH/Pt}$ represents the total energy of the Pt(100) slab after the adsorption of n hydrogen atoms,
E_{Pt} is the total energy of the clean Pt(100) slab and E_{H_2} is the total energy of the isolated H_2 molecule.

3. RESULTS

3.1 Lattice parameter of platinum

Platinum is a metal that crystallizes in the face-centered cubic (fcc) system. Understanding the lattice parameter of this crystal is crucial, as it provides data that is highly valuable for all our calculations. To determine this lattice parameter, we considered a three-dimensional crystal, assumed to be of infinite dimensions. We calculated the lattice energy for different parameter values to identify the one that minimizes the energy of the bulk. The calculated lattice parameter of platinum is equal to 4.003Å. This theoretical value is slightly larger than the experimental value which is 3.924Å [13].

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Our result is however in good agreement with those found by Kokalf and Causa (1999) [14], Steckel et al., (2003) [15], by Crljen et al., (2003) [16], and by Moussounda et al., (2007) [10] which are respectively 3.98Å, 3.99Å, 4.00Å and 4.005Å.

3.2 Parameter of H_2 molecule

Two crucial parameters must be determined for the H_2 molecule: firstly, the length of the H-H bond, and secondly, the energy value of the molecule in the gas phase. Following the optimization of the molecular geometry, we obtained an H-H distance of 0.756Å, and the energy of the molecule was determined to be -31.795 eV. Our result for the H-H distance is in good agreement with the findings of Jiang et al., (2003) [17], Lai et al., (2005) [18], and Kresse et al., (2000) [19], which are respectively 0.752Å, 0.749Å, and 0.750Å. It is worth noting that our value is slightly larger than the experimental value, which is 0.741Å [20].

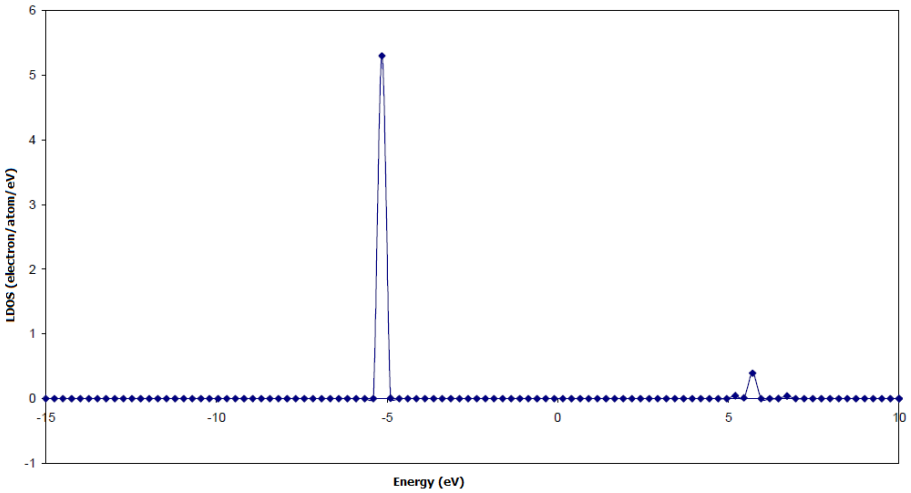

Figure 4: The figure represents the LDOS of H in the H_2 molecule in the gas phase.

This curve, in figure 4, indicates the presence of a prominent peak at -5.15 eV, representing the occupied state for the 1s orbital. Additionally, an unoccupied state is observed around 5.7 eV. It is noteworthy that in the study of the H_2 molecule, Moussounda (2006) [12] reported a significant peak at -4 eV, while Rakotovelo (2008) [21] observed a pronounced peak at -5.757 eV.

3.3 Adsorption of H_2 molecule

3.3.1 Configurations where the H-H direction is presented perpendicular to the surface plane

3.3.1.1 T1 configuration: adsorption in apical (T) site

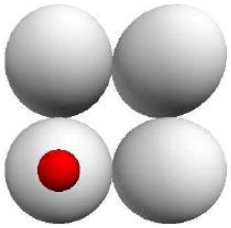

Figure 5: The figure presents the top view of T1 configuration. Red sphere is a hydrogen atom and grays spheres are platinum atoms.

For this T1 configuration, the H_2 adsorption energy is approximately -43meV. This value of the adsorption energy is quite low and we can think that the molecule is only weakly bound to the surface. For this configuration, the H-H distance is only slightly modified (0.771Å) compared to the free molecule (0.755Å). The integrity of the molecule is therefore preserved. On the other hand the distance between hydrogen and the closest platinum is 2.241Å. This distance, which is also the distance of the molecule from the surface plane, shows that the molecule is pushed upwards relative to the surface plane. Which confirms the low value of the adsorption energy for this configuration and therefore this configuration is very unstable. We can therefore think of a physical adsorption which is characterized by a low value of the adsorption energy associated with a long-range interaction.

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3.3.1.2 B1 configuration: adsorption in bridged (B) site

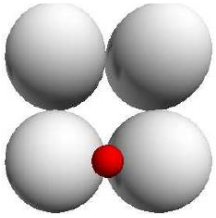


Figure 6: The figure presents the top view of B1 configuration. Red sphere is a hydrogen atom and grays spheres are platinum atoms.

For this B1 configuration, the H_2 adsorption energy is approximately -21meV. This value of the adsorption energy is very small, which makes us think that the molecule is only very weakly bound to the surface. For this configuration, the H-H distance almost remained unchanged after adsorption of the molecule. It is 0.761Å for the adsorbed molecule and 0.755Å for the free molecule. The distance of the molecule from the surface plane is approximately 2.413Å. The molecule is then very far from the surface when the system is stabilized and this fact is probably linked to the low adsorption energy of the molecule for this configuration. In this case we also have physisorption.

3.3.1.3 H1 configuration: adsorption in hollow (H) site

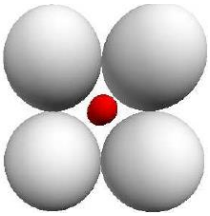
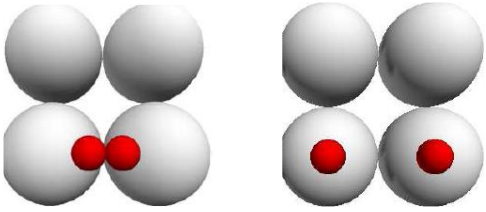


Figure 7: The figure presents the top view of H1 configuration. Red sphere is a hydrogen atom and grays spheres are platinum atoms.

For the H1 configuration, the strongly positive value (+0.71eV) of the adsorption energy leads us to conclude that the configuration is not stable. For this configuration, the H-H distance is significantly modified. It went from 0.755Å, for the isolated molecule, to 1.239Å. Molecular adsorption in this configuration is unstable. Which also confirms the positive value of the adsorption energy.

3.3.2 Configurations where the H-H direction is presented parallel to the surface plane

3.3.2.1 B2 configuration: adsorption in bridged (B) site



(**a**) (**b**)

Figure 8: The figure presents the top view of B2 configuration. (**a**) Initial configuration. (**b**) After geometric optimization. Red sphere are hydrogen atoms and grays spheres are platinum atoms.

For this configuration, the H-H distance increased from 0.755Å for the free molecule to 2.752Å for the system after optimization of the geometry. We notice that this configuration was stabilized when the two hydrogen atoms separated and were each stabilized practically in two apical sites neighboring the bridged site where the H_2 molecule was initially located. The distance between each H atom and the nearest neighbor platinum atom is 1.573Å.

The fact that the molecule is dissociated is confirmed by the adsorption energy of the molecule which is -0.780eV which corresponds to -0.39eV per H atom, this value is very close to that of the adsorption energy of a hydrogen atom at the apical site. In this case, it is a chemical adsorption which is short-range but has a fairly high adsorption energy.

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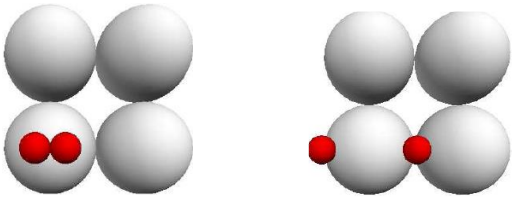
3.3.2.2 T2 configuration: adsorption in apical (T) site



(**a**) (**b**)

Figure 9: The figure presents the top view of T2 configuration.
(a) Initial configuration. (b) After geometric optimization.
Red sphere are hydrogen atoms and grays spheres are platinum atoms.

After optimization, the H_2 molecule which was located apically dissociates to give two H atoms which join two bridged sites neighboring the apical site where the molecule was initially located. The distance between each H atom and the nearest neighbor platinum atom is about 1.754Å and the adsorption energy of the molecule is -1.18eV, which corresponds to -0.59eV per H atom.

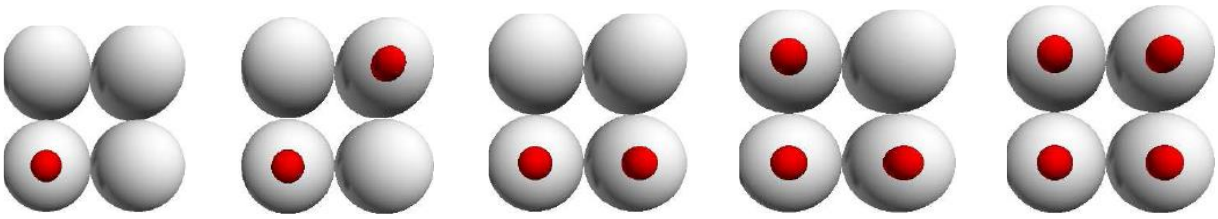
We notice that when the H_2 molecule is parallel to the surface, the molecule always tends to dissociate and we then witness a dissociative adsorption of H.

3.3.3 Conclusion on the adsorption of the H_2 molecule: During the study of the adsorption of the H_2 molecule on a Pt(100) surface, we observed two very distinct cases depending on whether the molecule is presented parallel or perpendicular to the plane of the latter. When the axis of the molecule is perpendicular to the plane of the surface, the molecule form a weak bond or form an unstable bond with the surface. The forces responsible for these weak bonds are forces of type Van Der Waals. When the axis of the molecule is parallel to the surface, the two atoms tend to dissociate. These effects of the orientation of the molecule relative to the surface on adsorption have already been reported by many researchers [22, 23, 24].

3.4 Adsorption of H atoms

3.4.1 Adsorption of H atoms with different coverage rates

3.4.1.1 Apical (T) sites: Descriptions of the studied configurations are presented in figure 10.



(a) (b) (c) (d) (e)

Figure 10: The figure represents the configurations studied for adsorption at apical sites.
(a) coverage of 0.25, (b) coverage of 0.5, (c) coverage of 0.5, (d) coverage of 0.75, (e) coverage of 1.
The little red sphere represents a hydrogen atom and the gray sphere represents a platinum atom.

Adsorption energies and inter-atomic distance calculated are summarized in table 1. From these results, we notice that the adsorption energies are of the same order of magnitude for the different coverage rates. Our results are in good agreement with those of Moussounda et al., (2007) [10] that are respectively -0.39eV, -0.40eV, -0.35eV and -0.35eV for coverage rates 0.25, 0.5, 0.75 and 1. Note, however, that for the coverage rate 0.5 we studied the two possible configurations and that we found different energies for the two configurations. Moussounda did not mention whether these two configurations gave the same energy or not. The differences in value may come from the fact that we took a slab of 3 layers and a cut-off energy of 350eV while the results of Moussounda et al., (2007) [10] are obtained with a slab of 4 layers and a cut-off energy of 400eV. Moussounda's results (2007) [10] could therefore be more precise than ours.

Table 1: Adsorption energies and inter-atomic distances for adsorption of H at apical sites.

Coverage	**(a) 0.25**	**(b) 0.5**	**(c) 0.5**	**(d) 0.75**	**(e) 1**
Adsorption energy (eV)	-0.423	-0.435	-0.390	-0.387	-0.369
Distance H-Pt (Å)	1.574	1.573	1.574	1.572	1.574
		1.573	1.574	1.573	1.574
				1.573	1.574
					1.574

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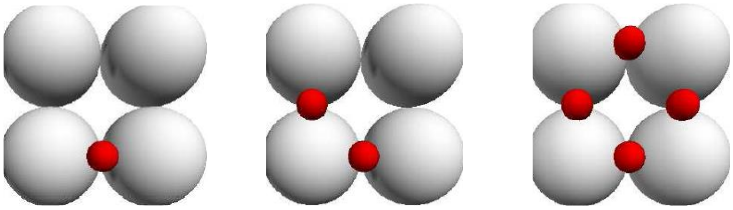
Likewise, the distances between hydrogen and the closest platinum that we found are also in good agreement with the results of Moussounda et al., (2007) [10] that are close to 1.572Å. Our results are around 1.574Å. Note that these values are slightly smaller than that found by Aryanpour et al., (2008) [25] who found a Pt-H distance of 1.68Å for the apical site.

3.4.1.2 Bridged (B) sites

For the bridged configuration, we studied the three configurations presented on the figure 11.



(**a**) (**b**) (**c**)

Figure 11: The figure represents the configurations studied for adsorption in bridged sites. (**a**) coverage of 0.25, (**b**) coverage of 0.5, (**c**) coverage of 1. The little red sphere represents hydrogen atom and the gray sphere represents a platinum atom.

The table 2 summarizes the adsorption energy and H-Pt distance.

Table 2: H adsorption energies and inter-atomic distances for adsorption of H at bridged sites.

Coverage	**(a) 0.25**	**(b) 0.5**	**(c) 1**
Adsorption energy (eV)	-0.62	-0.59	-0.57
Distance H-Pt (Å)	1.764	1.754	1.756
		1.754	1.756
			1.756
			1.757

For the coverage rate 0.25, the H-Pt distance we found is 1.764Å. This value is very close to those of Moussounda et al., (2007) [10] and M. Aryanpour et al., (2008) [25] who respectively found H-Pt distances of 1.763Å and 1.76Å for this configuration. For the coverage ratio 0.5, each of the H atoms is 1.754Å from the nearest neighbor Pt atoms. Our value is slightly smaller than that found by Moussounda et al., (2007) [10] which is 1.762Å for this coverage rate.

For coverage rate 1, the H-Pt distances are very close for the 4 H atoms. Three of the four H atoms are located 1.756Å from the closest Pt atoms and one is located 1.757Å from the closest Pt close neighbor. These values are in very good agreement with that of Moussounda et al., (2007) [10], which is 1.764Å for coverage rate 1.
For the bridged site, the H-Pt distances that we found are close to the values found by Moussounda et al., (2007) [10] and Aryanpour et al., (2008) [25].

3.4.1.3 Hollow (H) site

For Pt(100), the hollow site is considered to be the least stable in the works that we found in the literature. So in this work we will study only the adsorption of H for the coverage rate 0.25.

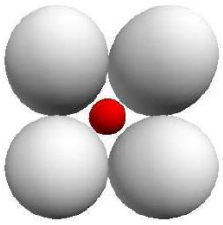


Figure 12: The figure represents the configuration studied for the adsorption of H in hollow site. The small red sphere represents a hydrogen atom and the gray sphere represents a platinum atom.

Table 3: H adsorption energy and inter-atomic distance for H adsorption in hollow site.

Coverage	**(a) 0.25**
Adsorption energy (eV)	-0.258
Distance H-Pt (Å)	2.074

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For coverage rate 0.25, we found an adsorption energy of -0.258eV. Moussounda et al., (2007) [10] did not report an energy value for this configuration but he concluded that this configuration is unstable. M. Aryanpour et al., (2008) [25] did not put forward a value for the adsorption energy for this configuration but mentioned that this configuration is the least stable among all the configurations. Our values also seem to lead to these observations since among the possible configurations, it is this configuration which has the lowest adsorption energy. Regarding the H-Pt distances for this configuration, we found a value of 2.074Å which confirms the value reported by M. Aryanpour et al., (2008) [25] who found 2.06Å.

3.4.2 Analysis of electronic structures

In the following sections we will study the electronic structures in order to identify other findings that can help us better understand the conclusions drawn from the adsorption energy values and the H-Pt distances. Our approach consists of comparing the electronic structure of H after adsorption on the Pt surface to that of H in the free H_2 molecule; then to compare the electronic structure of Pt of the surface after H adsorption to that of the clean surface.

3.4.2.1 Electronic structures of H

Apical site: Figure 13 represents the local density of states (LDOS) of the 1s band of H adsorbed in apical site and that of the 1s band of H in the free molecule.

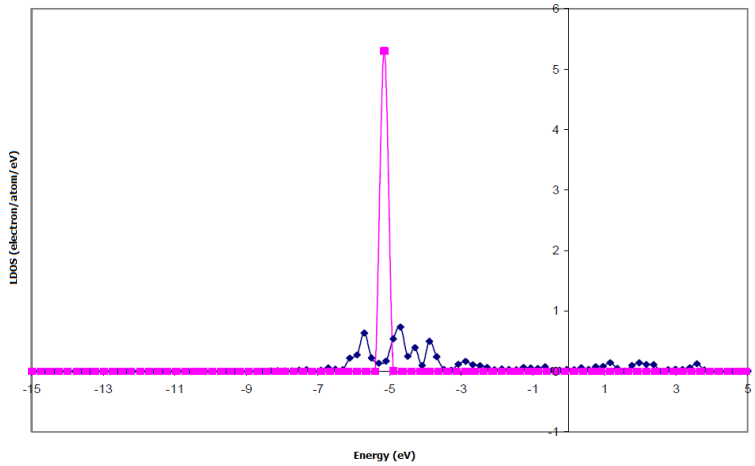

Figure 13: The figure represents the LDOS projected onto the 1s orbital of H at the apical site (blue curve) and in free H_2 (pink curve).

We find that the intense peak which is found at -5.15 eV for H in the free molecule has disappeared after adsorption of H on the surface. In place of this single peak, we observe states distributed continuously between -8.5 eV and 3.58eV with intermediate peaks at -5.7 eV, -4.69 eV, -4.29 eV and at -3.88eV. This change can be explained by a mixture of the 1s band of H and the Pt bands.

Bridged site: Figure 14 represents the LDOS of H adsorbed in a bridged site compared to that of H in free H_2.

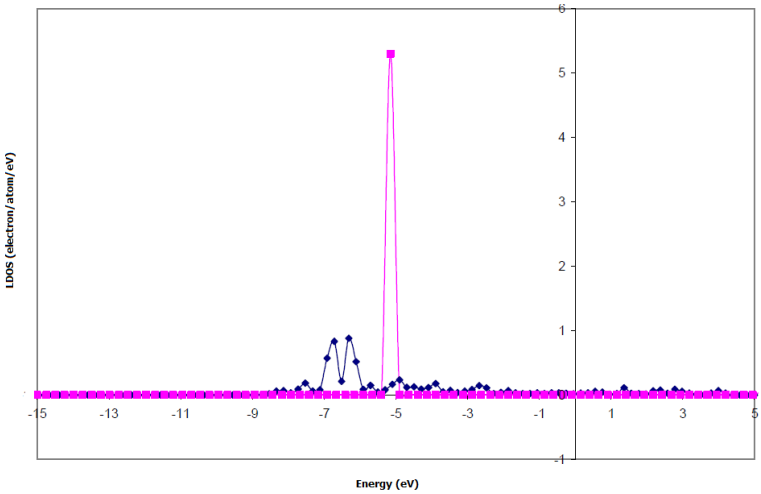

Figure 14: The figure represents the LDOS projected onto the 1s orbital of H at a bridged site (blue curve) and in free H_2 (pink curve).

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We observe that the peak at -5.15 eV observed for H in the free molecule has completely disappeared to give way to states distributed almost continuously between -8.5eV and 3.98eV. There is a mixture between the 1s band of H and the Pt band. Furthermore we can see that the center of gravity of the LDOS of H in bridge moves towards the lowest energies compared to that corresponding to H in H_2 free. We can then say that there is stabilization of states. This movement is less significant for the apical site.

3.4.2.2 Electronic structures of Pt

s-band of Pt at apical site : Figure 15 represents the LDOS of the s-band of Pt for the clean surface compared to the LDOS of the s-band of Pt after adsorption of H at the apical site.

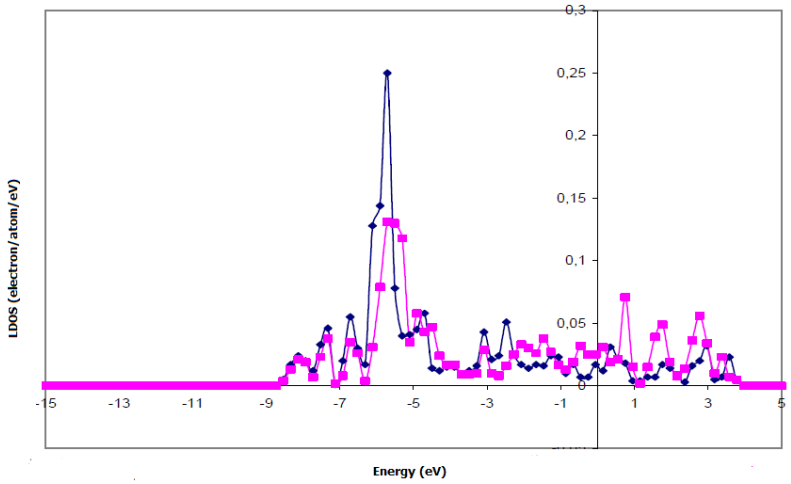

Figure 15: LDOS projected onto the s orbital of Pt after adsorption of H in a apical site (blue curve) and of Pt from the clean surface (pink curve).

We notice the appearance of resonances characterized above all by the increase in peak intensities, particularly at -5.7eV. This is explained by a mixture of the s band of Pt and the 1s band of H. We also note a decrease in the number of states from -2.07 eV and for all states above the Fermi level for the surface with H compared to the clean surface.

s-band of Pt at bridged site : Figure 16 represents the LDOS of the s-band of Pt for the clean surface compared to the LDOS of the s-band of Pt after adsorption of H in a bridged site.

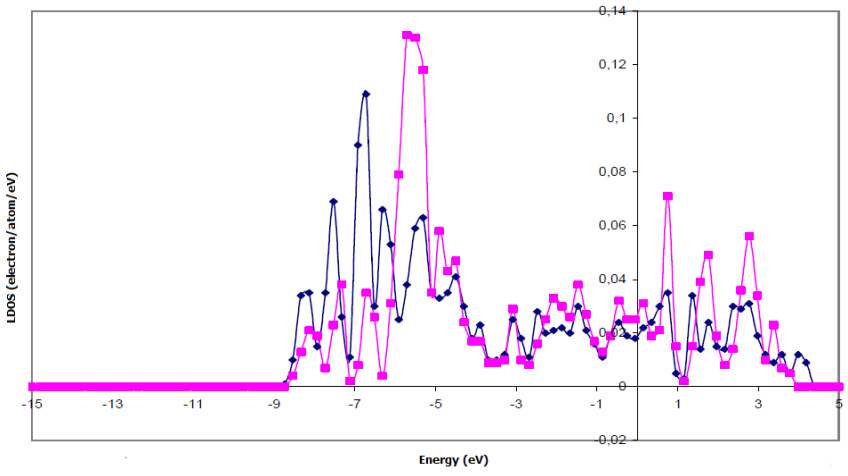

Figure 16: LDOS projected onto the s orbital of Pt after adsorption of H in a bridged site (blue curve) and of Pt from the clean surface (pink curve).

For the bridged site, the LDOS is much modified. We note a shift in the center of gravity of the band towards the lowest energies. In addition, resonance peaks appear at -7.5 eV, -6.7 eV and -6.3 eV. This change can be explained by a strong mixing between the s band of Pt and the 1s band of H. This change is more marked for the bridged site than for the apical site, it is therefore linked to the fact that the bridged site is more stable for H adsorption.

p_x-band of Pt at apical site : We present in figure 17 the LDOS of the p_x band of Pt for the clean surface compared to the LDOS of the p_x band of Pt after adsorption of H at the apical site.

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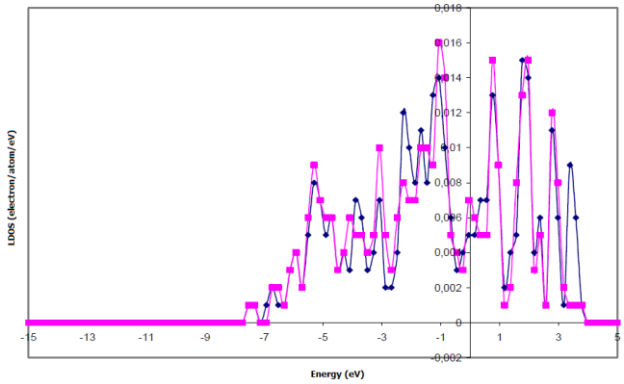

Figure 17: LDOS projected onto the p_x orbital of Pt after adsorption of H at the apical site (blue curve) and Pt from the clean surface (pink curve).

We note that the two curves almost coincide: there is therefore no change for the p_x band of Pt when H is adsorbed at the apical site. In other words, there is no interaction of the p_x band of Pt with the 1s band of H when the latter is at the apical site.

p_x-band of Pt at bridged site : We present in figure 18 the LDOS of the p_x band of Pt for the clean surface compared to the LDOS of the p_x band of Pt after adsorption of H in a bridged site.

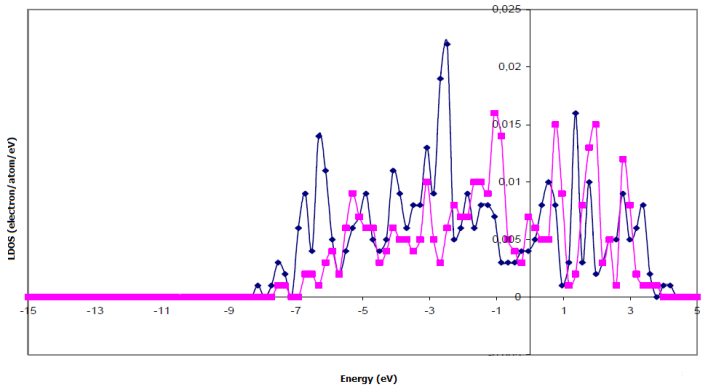

Figure 18: LDOS projected onto the p_x orbital of Pt after adsorption of H in a bridged site (blue curve) and of Pt from the clean surface (pink curve).

In the case where H is adsorbed at a bridged site, we observe a large modification of the LDOS of Pt compared to the LDOS of Pt on a clean surface. We note an intensification of the peaks located around -6.3 eV, -4 eV and -2.5 eV. These increases are due to resonances with the 1s state of H. We can conclude that there is much more interaction between the p_x band of Pt and 1s of H when H is in a bridged site than when H is in an apical site.

p_z-band of Pt at apical site : We present in figure 19 the LDOS of the p_z band of Pt for the clean surface compared to the LDOS of the p_z band of Pt after adsorption of H at the apical site.

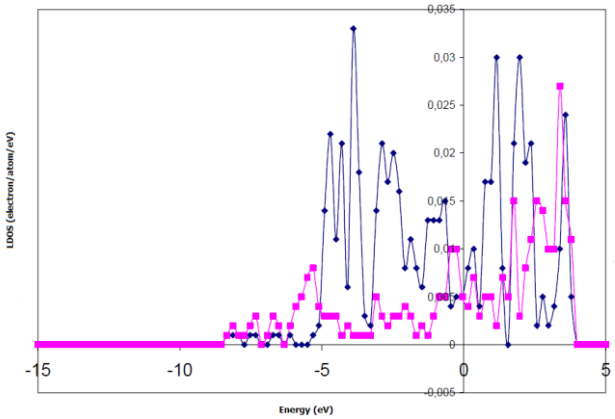

Figure 19: LDOS projected onto the p_z orbital of Pt after adsorption of H at the apical site (blue curve) and of Pt from the clean surface (pink curve).

We notice that for H at the apical site there is a large modification of the p_z band compared to the clean surface. The interaction of this p_z band of Pt with that of H(1s) induces intense peaks at -4.6eV, -3.8eV, -2.8eV, 1.16eV and 1.9eV.

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p_z-band of Pt at bridged site : We present in figure 20 the LDOS of the p_z band of Pt for the clean surface compared to the LDOS of the p_z band of Pt after adsorption of H in a bridged site.

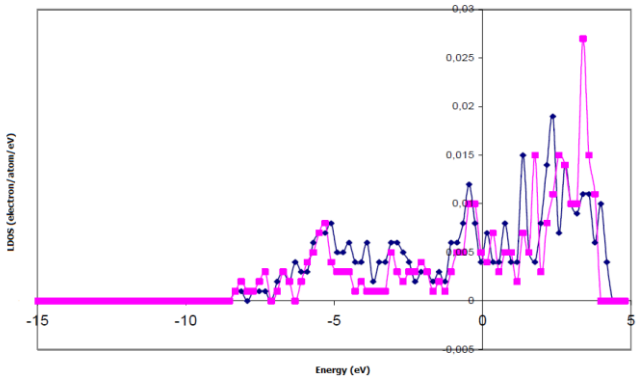

Figure 20: LDOS projected onto the p_z orbital of Pt after adsorption of H in a bridged site (blue curve) and of Pt from the clean surface (pink curve).

For H in a bridged site, we note a very slight modification of the LDOS between -8eV and +4eV: most of the peaks coincide but with different intensities, especially for 3.4 eV. We can conclude from figures 19 and 20 that when H is in the apical site, there is a strong interaction between the p_z band of Pt and the 1s band of H while in the bridged site, there is less interaction.

d_{z^2}-band of Pt at apical site : We present in figure 21 the LDOS of the d_{z^2} band of Pt for the clean surface compared to the LDOS of the d_{z^2} band of Pt after adsorption of H at the apical site.

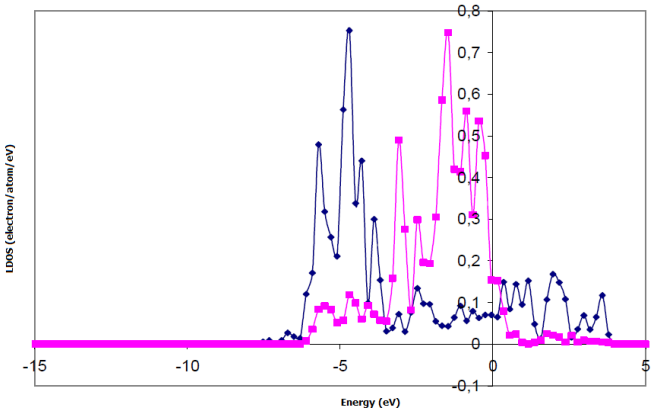

Figure 21: LDOS projected onto the d_{z^2} orbital of Pt after adsorption of H at the apical site (blue curve) and of Pt from the clean surface (pink curve).

We note a strong modification of the electronic structure of Pt after the adsorption of H at the apical site. We notice a shift towards low energies of the center of gravity of the LDOS: for the clean surface the curve was centered on -1.46 eV while for the surface with H it is around -4.69eV. This resonance at -4.69eV is due to an interaction with the 1s band of hydrogen.

d_{z^2}-band of Pt at bridged site : We present in figure 22 the LDOS of the d_{z^2} band of Pt for the clean surface compared to the LDOS of the d_{z^2} band of Pt after adsorption of H in a bridged site.

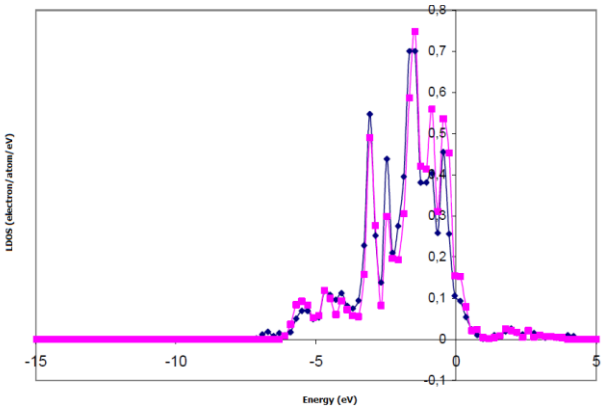

Figure 22: LDOS projected onto the d_{z^2} orbital of Pt after adsorption of H in a bridged site (blue curve) and of Pt from the clean surface (pink curve).

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For the bridged site, we notice that the two curves are almost merged and therefore that there is almost no modification of the d_{z^2} band of Pt when H is adsorbed in the bridged site. We can say from these two curves that at the apical site, the d_{z^2} band of Pt interacts with 1s of H while at the bridged site there is no interaction.

3.4.3 Evolution of H adsorption with high coverage rate: The problem we now want to elucidate is the following: if all the available sites are covered by H atoms, can adsorption still take place? To solve it we studied certain configurations with high coverage rates. Using a cell (2x2), for a high coverage rate, makes the calculation time too high. To further reduce the calculation time, we completed our study with a $(\sqrt{2} \times \sqrt{2})R45$ cell and we only relaxed the H atoms, the surface Pt atoms are fixed with all the other Pt atoms. The disadvantage of this choice is that we will also reduce the precision of the calculations.

Table 4: Adsorption energies for H adsorption with high coverage rates.

Configuration	Coverage	Adsorption energy (eV)
Hollow sites	1	-0.235
Bridged sites	2	-0.345
All sites occupied	4	0.565

For the hollow site with coverage rate 1, the adsorption energy is –0.235eV. This is in very good agreement with the results obtained with the cell (2x2) for the configuration rate 0.25 which is –0.258eV. We can then say that the results obtained with the two cells do not differ much. For the bridged site with coverage rate 2, the adsorption energy is –0.345 eV. This value is significantly lower in absolute value than for all the values obtained for the bridged configurations. Indeed, for the coverage rates 0.25, 0.5, 1, the adsorption energies are respectively: -0.615eV, -0.59eV and –0.56eV. The decrease in this adsorption energy is the sign of a repulsion between the adsorbed H atoms. The last configuration studied corresponds to the filling of all the sites of the cell $(\sqrt{2} \times \sqrt{2})R45$. In this case, 4 H are placed in bridged sites, 2 H are placed in apical sites and 2 H are placed in hollow sites in the $(\sqrt{2} \times \sqrt{2})R45$ cell. The coverage rate is 4. The adsorption energy per H atom is positive since it is 0.565eV. This configuration is therefore very unstable.

3.4.4 Conclusion on the study of H adsorption: The results of all the calculations show us that of the three sites studied (apical, bridged and hollow), the bridged site is the most stable for the adsorption of H while the hollow site is the least stable. We also note that generally for coverage rates of 0.25 to 1, the adsorption energy remains practically the same for the same site and the interaction between hydrogen atoms is not yet felt for this range of coverage rates. The differences between our results and those of other authors are relatively small (less than 5%). These differences in results could be explained on the one hand by the number of planes used to form the slab and on the other hand by the cutoff energy used for the simulations. However, our results for the hollow site are different from those of Moussounda et al., (2007) [10] but they rather seem to confirm those of Aryanpour et al., (2008) [25].

5. CONCLUSION

In this work, several aspects of the phenomenon of hydrogen adsorption both in its molecular form and in its atomic form, on a platinum (100) surface, were studied.
This adsorption phenomenon, the first step of a heterogeneous catalytic process, is studied based on density functional theory. The program used for the calculations is the DACAPO program. This code, based on density functional theory, makes it possible to determine numerous physical quantities of the system treated, in particular its total energy. It made it possible to determine many characteristic parameters of the system such as the lattice parameter for the platinum crystal, the bond length of the H_2 molecule.
The adsorption energy of the hydrogen molecule on a Pt(100) surface was calculated for different configurations and the study showed that the interaction of the molecule with the surface depends as well on the orientation of the molecule in relation to the surface than the type of site where this molecule is placed.
The adsorption of the hydrogen atom on the Pt(100) surface was studied for several configurations and for different coverage rates. The results of this study showed that:

- Bridged sites are more stable for H adsorption than apical sites. The least stable sites are hollow sites.
- For coverage rates not exceeding 1, the adsorption energy of the hydrogen atom on sites of the same type does not show any notable variation.
- When the coverage rate becomes large, especially from 1, the adsorption energy decreases.

The completion of this work allowed an introduction to ab initio calculations. It also allowed us to discover some of the many possibilities offered by the DACAPO program. The study of adsorption is in fact only one example of application of this code, it can be used for a very broad field, to name only the study of the magnetic properties of solids, the study of biological molecules. Modeling a chemical reaction on a surfaceis yet another possible application of this code.

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