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Investigation of LEPS potential energy surface for the interaction of a Pt(111) surface with a hydrogen atom

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Abstract

In this work, the identification of a potential energy surface between H atom and Pt(111) surface has been studied through the use of London-Eyring-Polanyi-Sato potential energy function (PEF). The energy values for the H–Pt(111) interaction calculated using density functional theory were used to determine the parameters of this PEF by using a nonlinear least-squares method. For this study, four symmetric sites on the surface were considered as a top site, bridge site, fcc-hollow site and hcp hollow site. It can be determined which sites on the Pt surface are penetration region, adsorption site or scattering site by defining the potential energy surface. It is found that both of the hollow sites of the surface are regions where H atom can penetrate directly to subsurface and it can be held easily on the surface.

***Keywords**: Potential energy surface, LEPS, Pt(111) surface, adsorption.*

Pt (111) yüzeyi ile hidrojen atomunun etkileşimi için LEPS potansiyel enerji yüzeyinin incelenmesi

Özet

Bu çalışmada, London-Eyring-Polanyi-Sato potansiyel fonksiyonunun kullanımı ile H atomu ile Pt (111) yüzeyi arasındaki potansiyel enerji yüzeyinin tanımlanması teorik olarak incelenmiştir. Yoğunluk fonksiyonel teorisi kullanılarak hesaplanan H – Pt(111) etkileşimine ait enerji değerleri, bu potansiyelin parametrelerinin lineer olmayan en küçük kareler yöntemi kullanılarak belirlenmesi için kullanılmıştır. Bu çalışma için, yüzeydeki dört simetrik alan, tepe bölgesi, köprü bölgesi, fcc- boşluk bölgesi ve hcp-

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boşluk bölgesi olarak düşünülmüştür. Potansiyel enerji yüzeyinin tanımlanmasıyla, hidrojen atomunun yüzeyde tutunabileceği ve alt yüzeye kolayca nüfuz edebileceği bölgeler tespit edilmiştir. Yüzeyin boş bölgerinin, H atomunun doğrudan alt yüzeye geçtiği ve H atomunun yüzey üzerinde kolaylıkla tutulabileceği bölgeler olduğu bulunmuştur.

Anahtar kelimeler: *Potansiyel enerji yüzeyi, LEPS, Pt(111) yüzeyi, adsorpsiyon.*

1. Introduction

The interaction of gas-phase H atoms with different metal surfaces has been theoretically studied to understand the adsorption mechanism of H atoms on metal surfaces [1-21]. As a result of these kind of researches, technologically important processes such as catalysis, corrosion effects on metal surfaces and hydrogen storage have been developed. The principle results of these studies include the characterization of the potential energy surfaces (PES) of metal surfaces in terms of reaction mechanisms with the H atom. Thus, various strategies based on the density functional theory (DFT) and quasiclassical calculation methods have been used. The use of these theoretical techniques has allowed the determination of symmetric surface sites suitable for adsorption, penetration, or scattering of H atoms.

According to the results of the investigation of the interactions of atomic and molecular hydrogen with Pt(111) as studied using DFT within the generalized gradient approximation (GGA), PES was found to be energetically and geometrically corrugated because of the surface atoms[1]. Furthermore, ab initio calculations of the interaction of H with Pt(111), Pd(111), and Ni(111) surfaces have been performed to obtain adsorption energies of H by using Vienna ab initio Simulation Package (VASP) code [2]. The results of these studies have allowed the determination of the adsorption energies and the adsorption heights for different sites on the Pt(111) surface [1, 2].

Through the use of a plane-wave and pseudopotential code DACAPO[3], potential energy values for the interaction of the H atom with Cu(111), Pt(111), and Pd(111) surfaces have been calculated and these describe adsorption and absorption scenarios of the H atom on/in the surface. It was found that fcc-hollow and hcp-hollow sites are suitable sites for the adsorption of the H atom on the surface. In other studies relating to the quantum mechanical behavior of the H atom on Cu(111) and Pt(111) surfaces, it was shown that hollow sites are suitable for the adsorption of the H atom onto the metal surface [4,5].

In addition, the interaction of the H atom with the Pt(111) surface was studied through the use of the DACAPO code for DFT calculations [6]. From these results, the adsorption energy of the H atom on the hollow site was computed to be approximately 2.7 eV at a height of 0.976 Å [6]. By using the VASP [7] to study the electronic properties of the H atom on vicinal Pt surfaces, it was concluded that the fcc-hollow site has a local energy minimum at its equilibrium height.

The selection of a suitable PEF for corresponding PESs is an important issue for quasiclassical and molecular dynamic studies. One of the most selected PEF for interatomic interactions, especially atomic and molecular hydrogen interaction with surface, is London-Eyring-Polanyi-Sato (LEPS) potential. For example, LEPS has previously been used to characterize the interaction of the H atom with Pt [1-11], Ni [12-15], and Cu [16-21] surfaces.

In this work, the LEPS PEF is used to describe PES for the interaction between the H atom and the Pt(111) surface and to determine reaction pathways for the penetration, adsorption, and scattering from sites on the Pt(111) surface. In the following section, the theoretical model and parameterization of LEPS is discussed and PES is fully described. Results are presented and discussed in the final section.

2. Methods and materials

The most important part of theoretical studies about surface structures and clusters formed by metal atoms is to determine the PEFs that accurately and precisely describe these systems. LEPS potential form [16] has been used for the study of the interaction of a gaseous atom (or diatomic molecule) with different metal surfaces and has previously been used to describe, in detail, the interaction of the H atom with a Pt(111) surface. PESs that describe the interaction between the H atom and Pt(111) surface need to be defined and analyzed. For this reason, it is important to determine the parameters of the LEPS function.

LEPS function, which include functions of Coulomb "Q" and exchange "J", given as:

$$\begin{aligned} V_{LEPS}\left(X_A, X_B, \{X_S\}\right) &= Q_{A,B} + Q_{A,S} + Q_{B,S} \\ &\quad - \left[J_{A,B}\left(J_{A,B} - J_{A,S} - J_{B,S}\right) + \left(J_{A,S} + J_{B,S}\right)^2 \right]^{1/2} \end{aligned} \tag{1}$$

Here, A, and B denote hydrogen atoms, and S represents all the surface atoms. X_A, X_B and $\{X_S\}$ are the position of hydrogen atoms and the surface atoms, respectively. “A,S” and “B,S” pairs of the subscripts stay for the interactions between hydrogen atoms and the surface atoms while “A,B” subscripts denotes the interaction between hydrogen atoms. Coulomb $Q_{A,B}$, Coulomb $Q_{A,S}$, exchange $J_{A,B}$ and exchange $J_{A,S}$ functions are given by;

$$Q_{A,B} = \frac{D_e}{4\left(1+\Delta_{A,B}\right)} \left\{ \left(3+\Delta_{A,B}\right) e^{-2\alpha_e\left(R-R_e\right)} - \left(2+6\Delta_{A,B}\right) e^{-\alpha_e\left(R-R_e\right)} \right\} \tag{2}$$

$$\begin{aligned} Q_{A,S} = \frac{1}{4\left(1+\Delta_{A,S}\right)} \Bigg\{ &\left(3+\Delta_{A,S}\right) \left(D_H e^{-2\alpha_H\left(r_s - r_H\right)} + \sum_{K=1}^{N} D_2 e^{-2\alpha_2\left(R_{A,S}-r_2\right)} \right) \\ &- \left(2+6\Delta_{A,S}\right) \left(D_H e^{-\alpha_H\left(r_s - r_H\right)} + \sum_{K=1}^{N} D_2 e^{-\alpha_2\left(R_{A,S}-r_2\right)} \right) \Bigg\} \end{aligned} \tag{3}$$

$$J_{A,B} = \frac{D_e}{4\left(1+\Delta_{A,B}\right)} \left\{ \left(1+3\Delta_{A,B}\right) e^{-2\alpha_e\left(R-R_e\right)} - \left(6+2\Delta_{A,B}\right) e^{-\alpha_e\left(R-R_e\right)} \right\} \tag{4}$$

$$J_{A,S} = \frac{1}{4\left(1+\Delta_{A,S}\right)}\left\{\left(1+3\Delta_{A,S}\right)\left(D_H e^{-2\alpha_H\left(r_s-r_H\right)} + \sum_{K=1}^{N} D_2 e^{-2\alpha_2\left(R_{A,S}-r_2\right)}\right)\right.$$
$$\left. -\left(6+2\Delta_{A,S}\right)\left(D_H e^{-\alpha_H\left(r_s-r_H\right)} + \sum_{K=1}^{N} D_2 e^{-\alpha_2\left(R_{A,S}-r_2\right)}\right)\right\} \quad (5)$$

Here, $R=|X_A - X_B|$ and $R_{A,S}=|X_A - X_S|$.

To find the parameters of the LEPS potential, energy values calculated using DFT (which is based on the postulates of the quantum mechanics of the H - Pt(111) interaction) were used. Thus, results from the study of the interaction of H with the Pt(111) surface by Ludwig and Vlachos [6] were used to fit the LEPS parameters by using a nonlinear least-squares method. In their work [6], potential energy values were calculated between the H atom and three different symmetry regions (a top, fcc-hollow, and bridge) of the Pt(111) surface by using the DFT method.

For the parameterization of the LEPS, a six-layered Pt(111) surface comprising 1092 Pt atoms with ABCA alignment (as shown in the Figure 1) was used for the face-centered cubic “fcc” surface structure. The lattice parameter of the Pt(111) slab was taken as 3.92 Å [22].

The top and side views of the symmetry sites on the Pt(111) surface are shown in Figure 1. The region between the two atoms on the first layer is known as the “bridge site.” The region where the surface atoms are located is known as the “top site”. The fcc-hollow site is at the center point of the unit triangle and the second layer surface atom is not located under this site. Besides, under the hcp-hollow site, where there is the second layer surface atom, lies the center point of the other neighbor unit triangle.

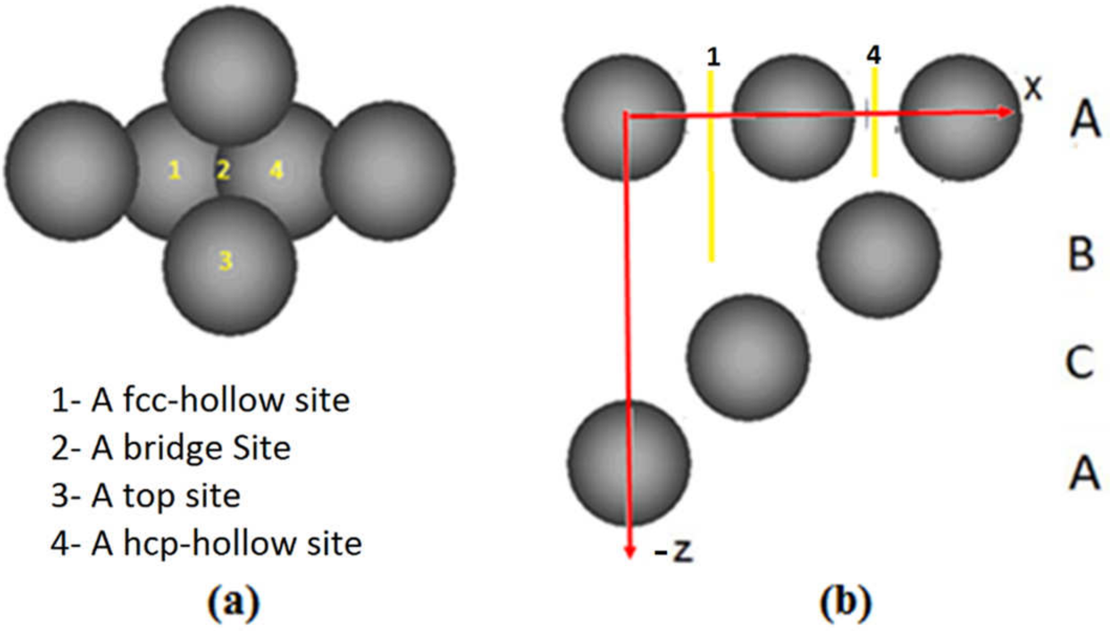

Figure 1. Symmetric sites on the Pt(111) surface with ABCA alignment a) top view and b) side view.

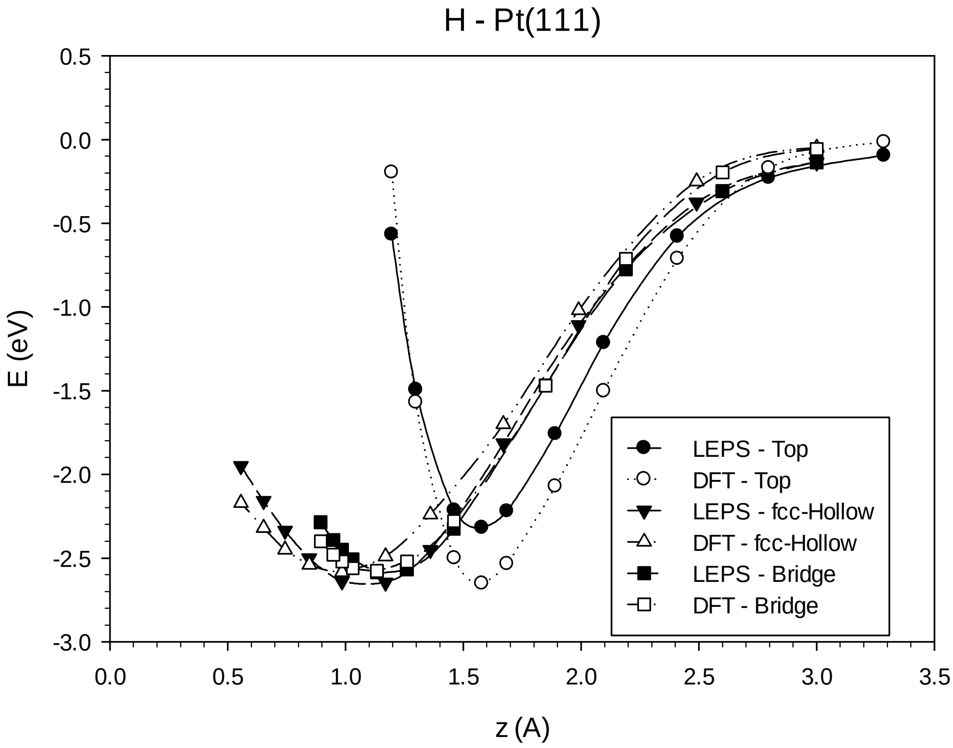

Figure 2. Energy values calculated using the LEPS function together with DFT energy values plotted as a function of z (height of an H atom over the Pt(111) surface) for three symmetric sites, namely, top site, fcc-hollow site, and bridge site.

The binding energies of H atom for top, bridge, and fcc-hollow sites are −2.312, −2.590, and −2.647 eV, respectively. The heights of the H atoms corresponding to the minimum binding energies for these sites are 1.6, 1.2, and 1.0 Å, respectively. For these regions, the DFT energy curves [6] and LEPS energy curves (depending on the height of the H atom over the Pt(111) surface) are shown for comparison in Figure 2. The above results are consistent with those presented in reference [6].

The LEPS parameters were obtained by fitting (using a nonlinear least-squares method) to the energy values obtained by DFT methods [6]. This was done for three symmetry regions, namely, top site, fcc-hollow site, and bridge site. The LEPS parameters obtained in this way are shown in Table 1. The root-mean-square (rms) error value for the determination of the parameters is 0.168.

Table 1. LEPS parameters obtained for H-Pt(111) interaction system. (rms value = 0.168).

$\Delta_{H,H} = 0.000$	$D_2 = 0.148$ eV	$\Delta_{H,Pt} = 0.346$
$D_e = 4.745$ eV	$D_H = 2.000$ eV	$R_H = 2.320$ Å
$\alpha_e = 1.900$ Å^{-1}	$\alpha_2 = 1.480$ Å^{-1}	$R_2 = 2.010$ Å
$R_e = 0.733$ Å	$\alpha_H = 1.040$ Å^{-1}	$N_{6s} = 0.670$

3. Results

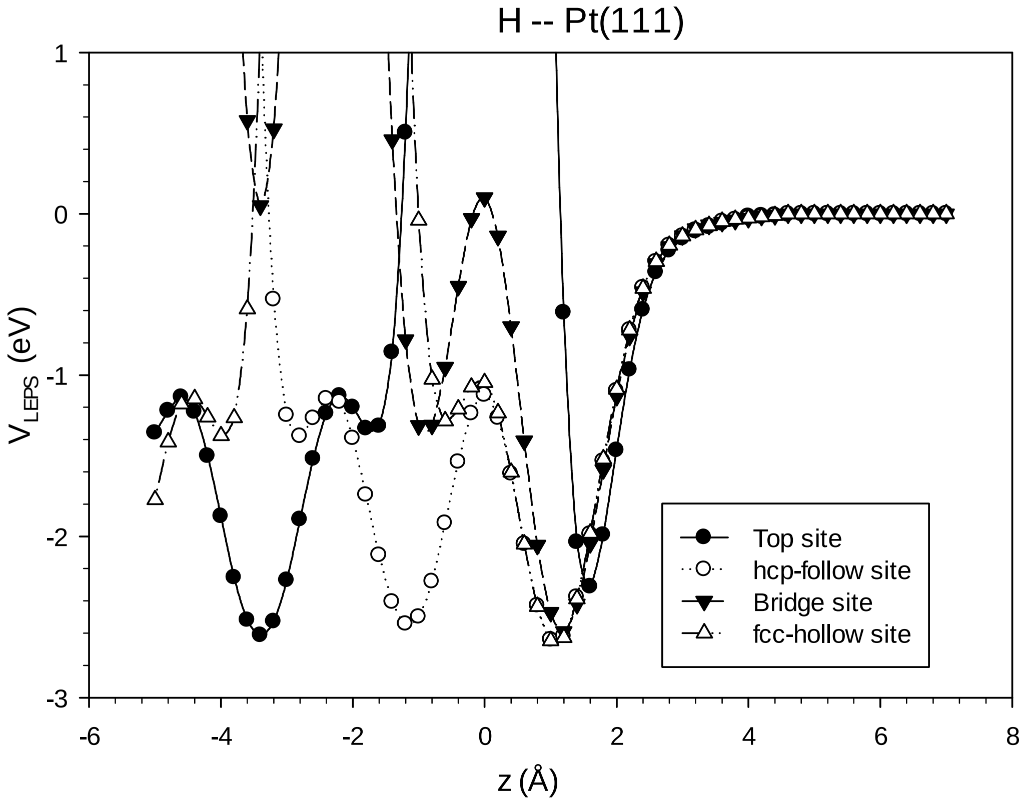

Figure 3. LEPS potential energy curves of a single H atom above and below four symmetric surface sites of the Pt(111) surface.

LEPS potential energy curves that are calculated as a function of the height z for the H atom on four different symmetric regions of the Pt(111) surface are shown in Figure 3. The binding energies of the H atom for the symmetric sites, top, bridge, fcc-hollow, and hcp-hollow are −2.312, −2.590, −2.647, and −2.641 eV, respectively. The heights of the H atoms corresponding to the minimum binding energies for these sites are calculated as 1.6, 1.2, 1.0 and 1.0 Å, respectively. These results are almost consistent with those presented in literature [2, 5, 6, 8] as shown as Table 2.

Table 2. Comparison of the results of interaction system of H- Pt(111) with previous studies.

	Sites			
	Atop	fcc-Hollow	hcp-Hollow	Bridge
z* (Å)	1.60	1.00	1.00	1.20
z (Å)	1.57 [2], 1.58 [6], 1.53 [8]	0.92 [2], 0.98 [6], 0.91 [8]	0.93 [2], 0.90 [8]	1.07 [2], 1.13 [6], 1.05 [8]
E* (eV)	−2.31	−2.65	−2.64	−2.59
E (eV)	−2.65 [6], −2.76 [8],	−2.55 [5], −2.58 [6], −2.49 [8]	−2.66 [8]	−2.58 [6], −2.68 [8]

*: results of this study.

The binding energies for bridge, fcc-hollow, and hcp-hollow sites on the surface at a height of 0 Å are calculated as 0.101, −1.048, and −1.123 eV, respectively. These results indicate that both of the hollow sites are regions where it is possible for the H atom to penetrate into the subsurface. By comparison, there is a minor potential energy barrier above the bridge site. Both of the hollow sites are suitable for adsorbing an H atom onto Pt(111). For an incident H atom, penetration into the subsurface and back scattering regions can be easily distinguished at a height of z = 0 Å, as indicated in Figure 3. From Figure 3, it can be seen that the potential energy barrier of the surface increases when the H atom approaches the surface over the top site.

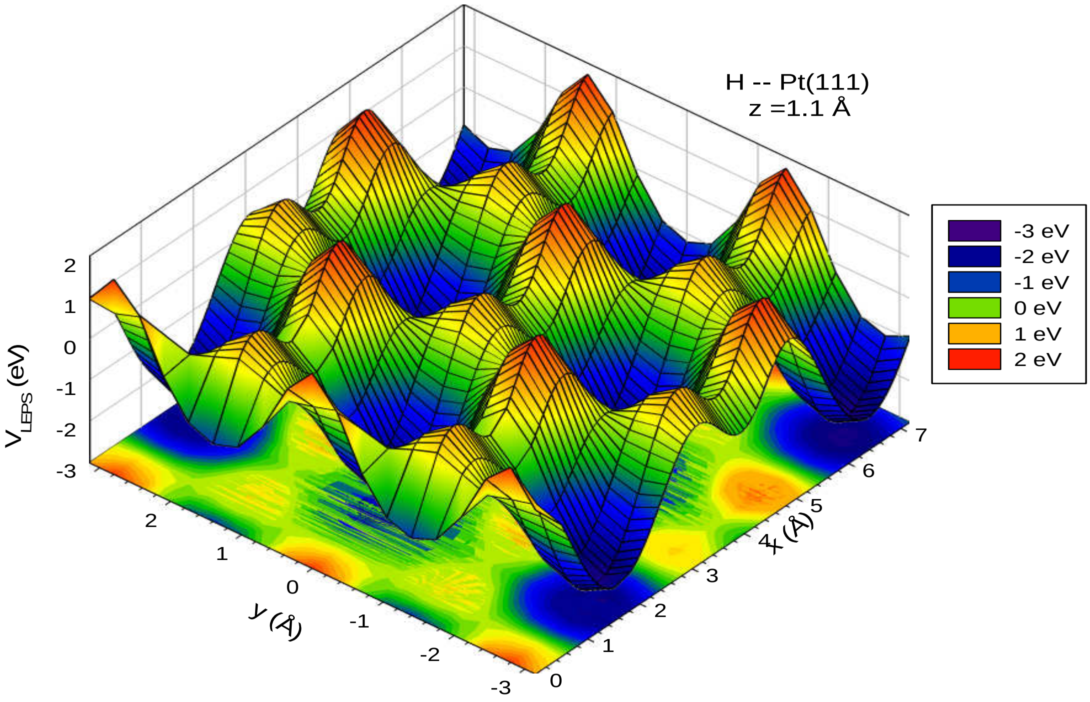

Figure 4. Three-dimensional counter plot showing the potential energy surface for an H atom at a height of 1.1 Å from the surface of Pt(111).

Figure 4 shows a three-dimensional counter plot of the potential energy surface for an H atom at a height of 1.1 Å from the Pt(111) surface. Regions that have the repulsive potential energy values at the maximum correspond to regions where surface atoms are located. However, regions where the potential surface energy is a minimum correspond to fcc-hollow and hcp-hollow sites. H atom approaching the surface can be scattered over the regions where the potential energy is a maximum or trapped at the sites associated with a minimum attractive potential energy surface. As the H atom approaches the surface, the effect of the repulsive force of the surface potential increases when the H atom is in the region of the bridge site. Besides, the regions where the energy is minimum can correspond to the path of movement of H atom over the surface between fcc-hollow and hcp-hollow sites.

Contour plots of the potential energy surfaces for different heights of the H atom over the surface are shown in Figure 5.

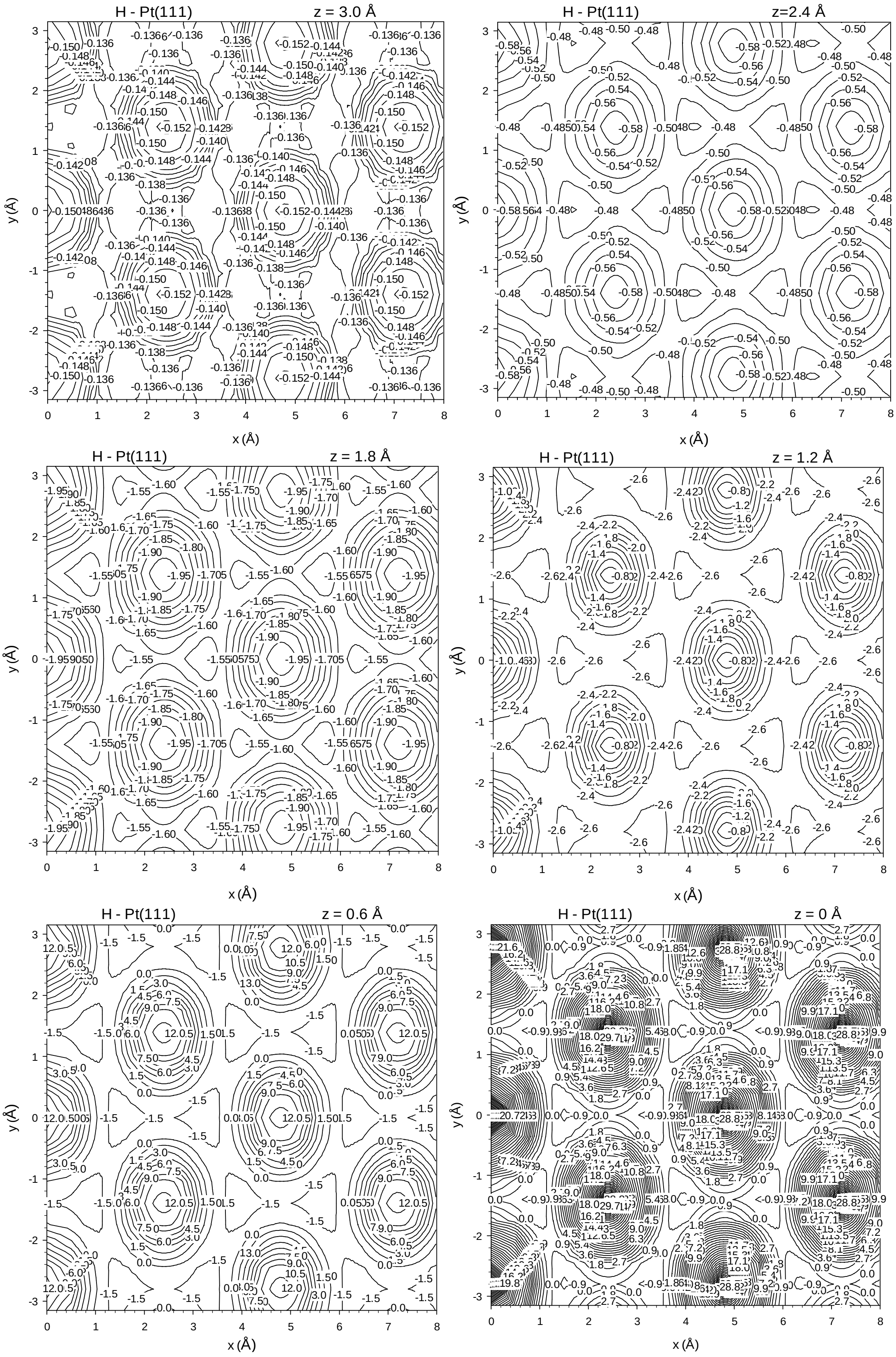

Figure 5. Contour plots of the potential energy surfaces for interaction of the H atom with Pt(111) surface at heights of z = 3, 2.4, 1.8, 1.2, 0.6 and 0.0 Å, respectively.

As the H atom approaches the surface from a height of 3 Å to 1.8 Å, it is seen that the potential attractive effect of the surface of the metal on the H atom increases, as indicated by Figure 5. This figure also shows that when the H atom approaches from a height of 1.8 Å to 1.2 Å above the surface, the attractive potential energy effect of the metal surface on the H atom over the bridge and hollow sites increases, whereas the impulsive potential energy effect of the metal surface increases over the top site. At a height of 0.6 Å above the surface, the H atom is exposed to a repulsive effect from the potential energy surface, as indicated in Figure 5.

It is clearly seen in Figure 5 that it is difficult for the H atom to pass to the subsurface over the bridge site due to the repulsive potential effect of the surface atoms. By comparison, the H atom can easily penetrate into the subsurface via the hollow sites. However, if an H atom approaches the surface with sufficient kinetic energy, then it is possible to penetrate into the subsurface from over the bridge site.

H atoms may be located at different heights or levels below the surface of the metal. For these conditions, contour plots of the potential energy surfaces have been calculated and are given in Figure 6. These results indicate that atoms can become trapped in the subsurface at depths between 0 Å and −3.0 Å. Figure 6 illustrates that the repulsive effect of the PES toward the H atom increases on the top sites of the second and third layers as a result of surface atoms. The distance between surface layers is 2.263 Å.

As indicated in Figures 3 and 7, it can be seen that it is possible for the H atom to pass from the hcp-hollow site to the second layer. It is also possible for the H atom to pass directly up to the third layer from the fcc-hollow site. It is important to note that the adsorption and penetration sites of the H atom onto to the Pt(111) surface are similar to those of Ni(100) and Cu(111) surfaces [12-15, 19-21].

Three-dimensional contour plots of the PES for the Pt(111) surface and the H atom at y = 0 Å and x = 0 Å are shown in Figure 7. Besides, symmetric sites were shown in Figure 7. These figures illustrate the effect of the potential energy surface on the H atom at different heights above the surface or at different depths between the surface layers.

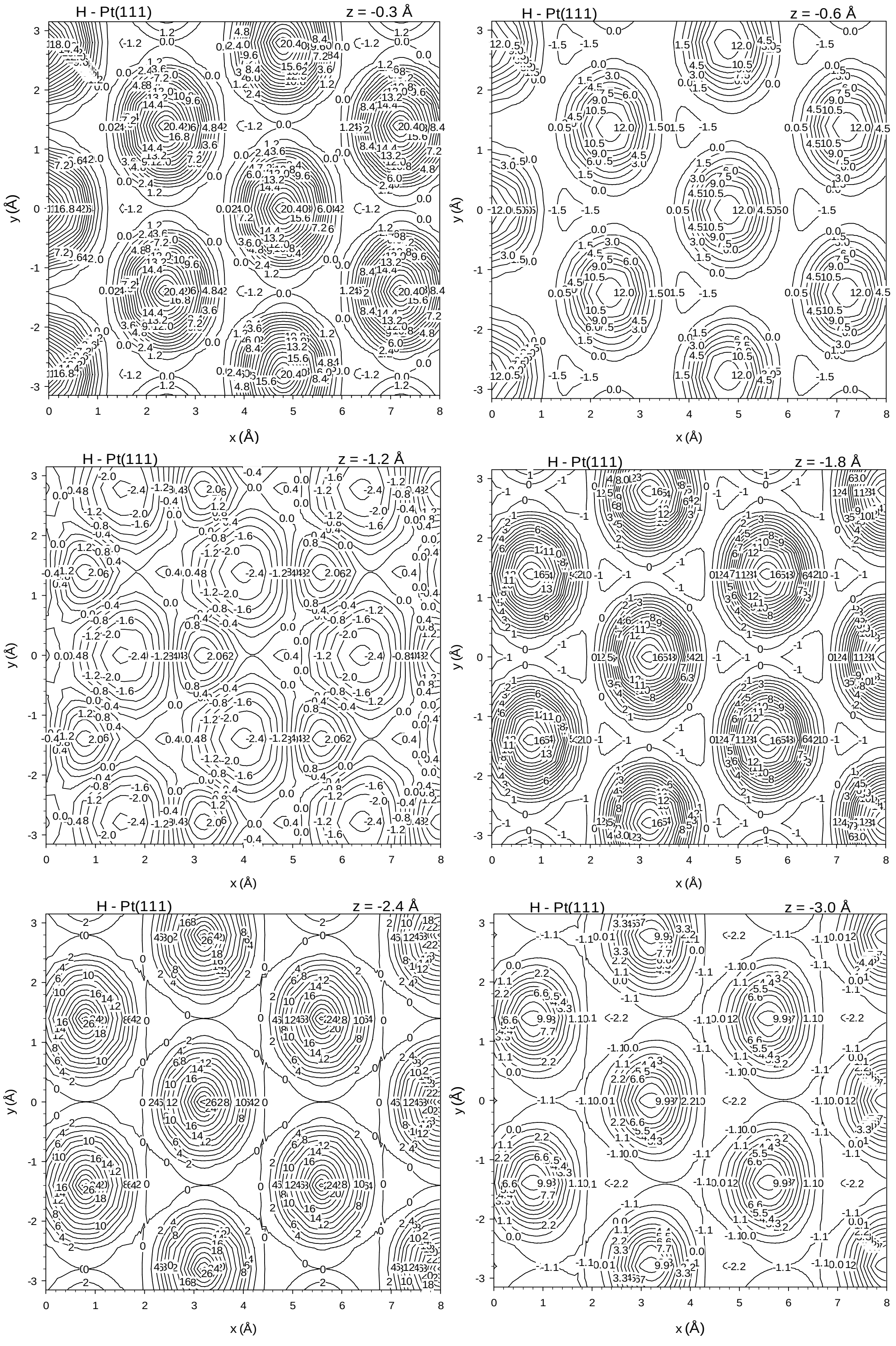

Figure 6. Contour plots of the potential energy surfaces for interaction of the H atom with Pt(111) surface at depths below the metal surface of −0.3, −0.6, −1.2, −1.8, −2.4 and −3.0 Å, respectively.

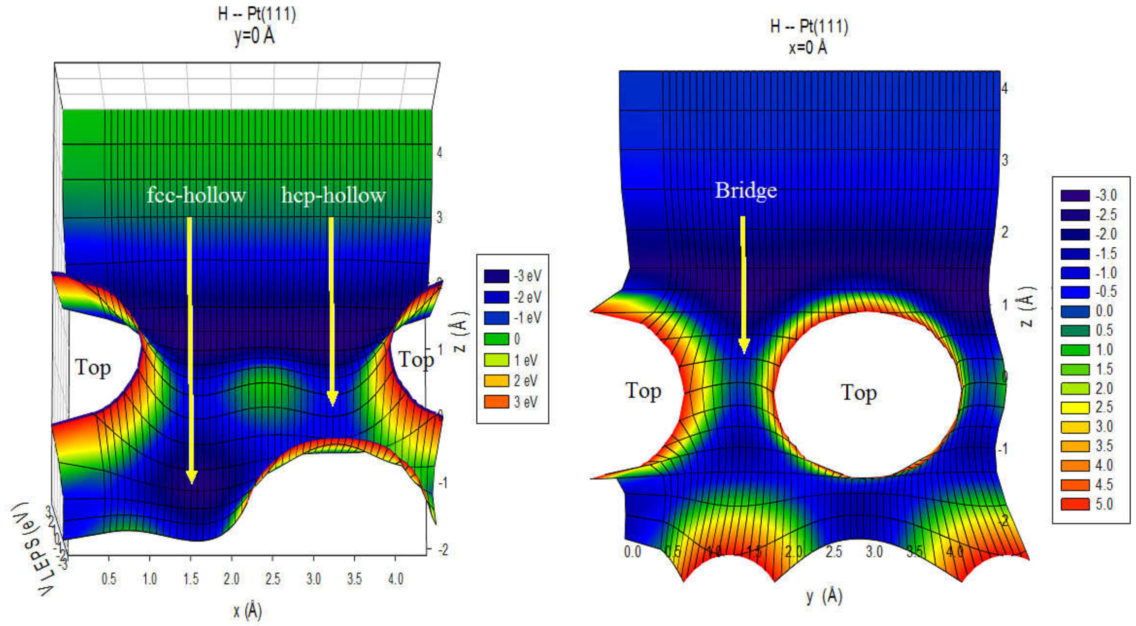

Figure 7. Three-dimensional contour plot of the potential energy surface for the H atom on the Pt(111) surface at y = 0 Å and at x = 0 Å.

Figure 7 shows there is almost no difference between the PES contours around fcc-hollow and hcp-hollow sites. An incident H atom approaching directly from the top site will be backscattered over the surface because of the high potential energy barriers around the top site. The potential energy surfaces exhibit approximately the same behavior for both hollow sites as shown in Figure 7. Moreover, it was shown in Figure 7 that there is a minor potential energy barrier for H atom where just over the surface.

4. Conclusions

In this work, PESs for the interaction between an H atom and Pt(111) metal surface were investigated. Thus, LEPS was chosen to represent the form of the potential as it accurately described the interaction of the surface with the H atom. Parameters of the LEPS potential were obtained by fitting DFT energy values for the interaction between H and the Pt(111) surface as described by Ludwig and Vlachos [6].

This investigation shows that the repulsive effect of the surface potential energy is high around the top site if the H atom is near the surface. Binding energy values were shown to be very close to each other on both of the hollow sites for the H atom. Furthermore, it was determined that there was almost same behavior of PES around fcc-hollow and hcp-hollow sites. It was also showed that for the condition of the H atom passing through the fcc-hollow site to the subsurface, the atom could proceed without encountering an energy barrier up until the third layer.

However, it could penetrate up to the second layer via the hcp-hollow site. Although H atom could be trapped in the subsurface via these reaction paths, it was also shown that it could be scattered from the top site. Therefore, it is seen that both hollow sites are appropriate for the adsorption of an H atom onto the metal surface. Finally, if the H atom has sufficient kinetic energy it can travel with paralel to surface from one hollow site to the other hollow site via the bridge site.

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