

# Dissociative adsorption of H<sub>2</sub> on the Pd(111) surface

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## Abstract

In the present work, we apply an ab initio approach to study the dissociative adsorption of a hydrogen molecule on the palladium (111) surface. Our approach is based on the density functional theory (DFT) with a generalized gradient approximation (GGA). The wave-functions are expanded in a plane-wave basis and the electron–ion interaction is described by ultrasoft pseudopotentials. Several pathways for the dissociative adsorption are studied in details. The potential energy surface for each path is determined. Spontaneous dissociation paths are found which have a very small barrier of about 70 meV. This agrees fairly well with the estimation based on the molecular beam experiments, 50 meV. We find that the geometric factor plays an important role: larger stretching of the hydrogen molecule bond leads to a higher barrier. Our results give also some indication for the existence of a precursor state.

**Keywords:** Adsorption; Dissociation; Surface; Transition-metal; Ab initio calculations; Palladium; Hydrogen

## 1. Introduction

Since the advent of the Car–Parrinello method [1], considerable progress has been made in ab initio calculation methods during the last ten years [2–5]. The Car–Parrinello method and its variants are all based on the following key ingredients: a plane-wave basis which allows for an easy calculation of the Hellmann–Feynman forces, first-principle pseudopotentials [6–12] which provide a convenient description of the electron–ion interaction, and the efficient direct optimization of the Hamiltonian either by

the Car–Parrinello method or by conjugate-gradient techniques [2–5]. The original method proposed by Car and Parrinello has been quickly proven very successful for studying semiconductors [2]. Recent advances in the methodology, i.e., ultrasoft pseudopotentials [13] and Fermi surface broadening [14] by using the finite temperature density functional theory [15] allow now to extend the method to study metallic systems and especially transition metals. This opens very promising perspectives for studying some fundamental problems in heterogeneous catalysis by ab initio calculations.

In the present work, the dissociative adsorption of H<sub>2</sub> on the Pd(111) surface is addressed. The interaction of hydrogen with palladium has

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attracted much attention for many years owing to the importance of Pd in many applications, e.g., catalysis of hydrogenation reactions (see, e.g., Refs. [16–18]). The dissociative adsorption of  $H_2$  is the first elementary step of these reactions. A large amount of work has been devoted to hydrogen–palladium systems by both experimental [16–32] and theoretical approaches [33–46]. Much experimental information is now available for these systems. This makes them quite ideal candidates for thorough theoretical investigations. Up to now, most theoretical efforts have been focused on the chemisorption of atomic H on different low-index surfaces [37–44], i.e., the final structure of already dissociated adsorbates on the surfaces. Only very recently, the whole process of the dissociative adsorption starts to be studied by theoretical approaches [45–58]. In this work, we examine a variety of pathways for the dissociative adsorption of  $H_2$  on the Pd(111) surface. By determining two-dimensional cuts through the six-dimensional potential energy surface (PES), we obtain very detailed information about the different pathways examined. The PES is the basis for understanding how the dissociative adsorption takes place dynamically. We will also discuss a very controversial topic: the possible existence of the precursor state.

## 2. Theoretical approach

Our approach is based on density functional theory [59,60]. Although the local density approximation (LDA) has been very successful for many applications, it has been shown that gradient corrections have to be invoked to determine accurately the dissociation barrier [46]. In this work, we use the exchange–correlation functional with a generalized gradient approximation (GGA) proposed by Perdew and Wang [61]. To avoid the instability coming from the level crossing and quasi-degeneracies in the vicinity of the Fermi level in metallic systems, fractional occupations of the eigenstates are allowed. This

can be done by using finite temperature density functional theory where the free energy is the variational functional [15]. In this way, the Fermi surface can be smeared by Gaussian or Fermi–Dirac broadening [14]. The Kohn–Sham equation [60] is solved numerically by a double iteration procedure. First, a preconditioned conjugate-gradient method [2–5] is applied, for one band each time, to improve the eigenvalues and wave functions at a fixed potential. Once all the considered bands are swept, a subspace diagonalization among these bands is made. Then the Fermi energy, eigenlevel occupancies, charge density, and potential are updated using an efficient mixing technique. The band-by-band minimization and the subspace diagonalization alternate until convergence is reached. The electron–ion interaction is modelled by pseudopotentials. Optimized non-local ultrasoft pseudopotentials are used. The pseudopotential optimization procedure has been described elsewhere [12]. For systems of large size, e.g., more than 15 atoms, the real space projection technique proposed by King-Smith et al. [62] to handle the non-local part of the pseudopotential furnishes a considerable gain in computational efficiency. All the above features of the computation techniques are implemented in the recently developed Vienna ab-initio simulation program (VASP). A more detailed description of the program can be found in the paper by Kresse et al. [3–5]. This approach has been applied successfully to a variety of problems in condensed matter physics including the study of the chemisorption of H on the Pd(111) surface and the dissociative adsorption of  $H_2$  on Rh(100) [44,57,58,63–66].

## 3. Computational details

In our approach, the electron–ion interaction is described by the ultrasoft pseudopotentials proposed recently by Vanderbilt [13]. The new feature of such pseudopotentials is the use of

short range augmentation functions which are defined as

$$Q_{ij}(\mathbf{r}) = \phi_i^{\text{AE}}(\mathbf{r})\phi_j^{\text{AE}}(\mathbf{r}) - \phi_i^{\text{ps}}(\mathbf{r})\phi_j^{\text{ps}}(\mathbf{r}) \quad (1)$$

where  $\phi^{\text{AE}}(\mathbf{r})$  and  $\phi^{\text{ps}}(\mathbf{r})$  are respectively all-electron and pseudo wave functions. In practice,  $\phi^{\text{AE}}(\mathbf{r})$  is pseudized by using a high-quality norm-conserving pseudo-wave-function. In Vanderbilt's ultrasoft pseudopotentials, several reference energies can be included. In this work, an ultrasoft pseudopotential for palladium has been generated from the reference electron configuration  $4d^9 5s^1 5p^0$ . For s and p components, norm-conserving pseudopotentials are constructed at the following cut-off radii and reference energies:  $R_{c,s} = 1.1113 \text{ \AA}$  and  $R_{c,p} = 1.4288 \text{ \AA}$ ;  $\varepsilon_s = -4.63 \text{ eV}$  and  $\varepsilon_p = -1.36 \text{ eV}$ . For the d-component, an ultrasoft pseudopotential is generated at two reference energies:  $\varepsilon_{d,1} = -6.93 \text{ eV}$  and  $\varepsilon_{d,2} = -8.16 \text{ eV}$  with a cut-off radius  $R_{c,d} = 1.4288 \text{ \AA}$ . The pseudized augmentation function is generated at the same reference energies with a cut-off radius of  $1.0584 \text{ \AA}$ . The ultrasoft pseudopotential of hydrogen is generated from the reference electron configuration  $1s^1 2p^0$  at the cutoff radius  $R_c = 0.6615 \text{ \AA}$  with reference energies  $\varepsilon_{s,1} = -6.36 \text{ eV}$ ,  $\varepsilon_{s,2} = -9.52 \text{ eV}$ , and  $\varepsilon_p = -3.40 \text{ eV}$ . The pseudized augmentation function is generated with a cut-off radius equal to  $0.4233 \text{ \AA}$ .

In the present work, plane waves with a cut-off energy equal to  $200 \text{ eV}$  are used to expand wave-functions. Gaussian smearing with a width  $\delta = 0.4 \text{ eV}$  is used for the fractional occupancy of eigenstates. The result corresponding to the zero temperature can be obtained by taking the limit  $\delta \rightarrow 0$  analytically [14]. To model surfaces, we adopt the slab supercell approach. All the calculations presented in this work are made on a slab containing five palladium layers. A vacuum space corresponding to 5 ideal Pd layers is used to avoid the interaction between the slab and its periodic images. Our previous work has shown that well converged results can be obtained for this system size. During the study of the dissociative

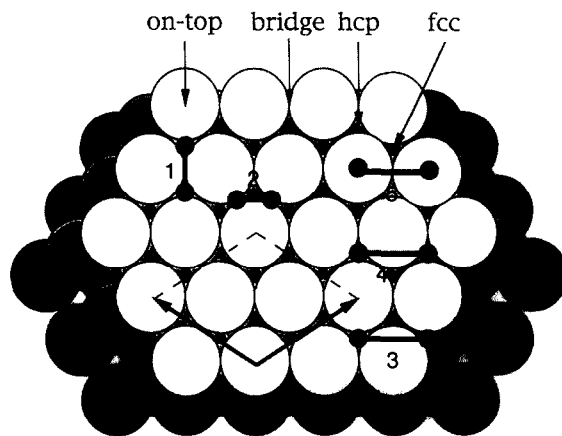


Fig. 1. Schematic presentation of a (111) surface showing the different adsorption sites and dissociative adsorption pathways: (1) fcc-hcp path, (2) bridge-bridge path, (3) fcc-fcc path, (4) hcp-hcp path, (5) top-top path.

adsorption of  $\text{H}_2$ , the Pd slab is frozen at its bulk structure since we have seen, in previous works [44,57,58], that the relaxation of the substrate has only a negligible influence on the adsorption energies. For the bulk lattice constant, our approach including GGA gives  $a = 3.95 \text{ \AA}$ , which is in good agreement with the experimental value of  $3.89 \text{ \AA}$  [67]. A  $\sqrt{3} \times \sqrt{3}$  surface cell has been used (see Fig. 1). Hence, each layer contains three Pd atoms. This choice is made in order to get the  $c(\sqrt{3} \times \sqrt{3})R30^\circ$  chemisorption pattern after the dissociation of  $\text{H}_2$  which is shown to be a stable structure at low temperatures [25,26]. The special k-points method proposed by Monkhost and Pack [68] is applied to carry out the Brillouin zone integration. A  $5 \times 5 \times 1$  grid is used.

#### 4. Results and discussions

In its most general form, the potential energy surface for the dissociative adsorption of  $\text{H}_2$  on Pd(111) is a six-dimensional hypersurface. Actually, the complete determination of such a hypersurface with six variables is still a very heavy computational task. Therefore, we have to appeal to our chemical intuition for selecting

some plausible low-energy paths in a more restricted space. The dissociation process will cost less energy if the bond breaking of the hydrogen molecule is accompanied by simultaneous bond forming between the adsorbate and the substrate. From this argument, it is believed that the pathways in which the hydrogen molecule remains essentially parallel to the surface are the energetically favorable ones. In their very recent work on the dissociative adsorption of  $H_2$  on Pd(100), Wilke and Scheffler [56] have shown that a 'cartwheel rotation' (a rotation moving the hydrogen molecule out of a plane parallel to the surface) gives rise to a sharp increase of energy near the transition state (TS). Hence, in this work we will restrict ourselves to consider only the paths in which the hydrogen molecule approaches the surface with its molecular axis parallel to the surface.

Fig. 1 is a schematic top view of the Pd(111) surface. The high-symmetry adsorption sites are indicated in this figure. There are two types of threefold sites: one called the fcc site, the other the hcp site. The difference between them is that there is a palladium atom below the hcp site in the second layer and below the fcc site in the third layer (i.e., an adatom placed at the fcc site continues the bulk lattice). In a recent work [44], we have studied in detail the chemisorption of atomic H on these sites. The two types of threefold sites have nearly the same energetic stability. The stability of a site correlates with

its coordination number: the larger the coordination number, the more stable the site. In the present work, we consider five different pathways for the dissociative adsorption. In Fig. 1, the destination configurations of the different paths are also indicated, i.e., a given path starting from a large distance (about 3 Å) above the surface and ending at the corresponding destination configuration. We name the paths by the end-destinations of the dissociated atoms, i.e., path 1 is called fcc–hcp, path 2 bridge–bridge, path 3 fcc–fcc, path 4 hcp–hcp, and path 5 top–top.

First, we have determined the adsorption energies and the geometries of the different end-configurations. The results are given in Table 1. As we have found previously [44], the threefold sites (fcc and hcp) are the most stable ones. The lateral H–H interaction on Pd(111) is repulsive. This explains why the fcc–hcp configuration is less stable than the fcc–fcc or hcp–hcp one since the H–H distance in the former is much shorter. The adsorption on the top–top configuration is slightly endothermic and exothermic on all the other configurations.

In Fig. 2, the PES for the fcc–hcp path is given. The plot given here is obtained by interpolation from 72 calculated points scanning different bond lengths of  $H_2$ ,  $d_{H-H}$ , and the heights above the surface,  $h_H$ . The PES for this path has a classical elbow-form. A saddle point is found at  $d_{H-H} = 0.78$  Å and  $h_H = 2.06$  Å. At

Table 1  
Adsorption energies,  $E_{ad}$ , and geometries of the end-configurations,  $\theta = (2/3)ML$

Configuration	fcc–hcp	Bridge–bridge	fcc–fcc	hcp–hcp	Top–top
$E_{ad}$ (eV/atom–H)	0.421	0.265	0.573	0.520	–0.007
$h_H$ (Å)	0.82 <sup>a</sup> ; 0.83 <sup>b</sup>	1.04	0.84	0.83	1.55
$d_{H-H}$ (Å)	1.61	1.40	2.79	2.79	2.79
$d_{H-Pd}$ (Å)	1.807 <sup>a</sup> ; 1.812 <sup>b</sup>	1.74	1.82	1.81	1.55

$$E_{ad} = (E[Pd(111)] + E[H_2] - E[H_2/Pd(111)]) / N_H$$

$h_H$ : height of H to the top Pd layer.

$d_{H-H}$ : H–H distance.

$d_{H-Pd}$ : H–Pd distance.

<sup>a</sup> fcc site.

<sup>b</sup> hcp site.

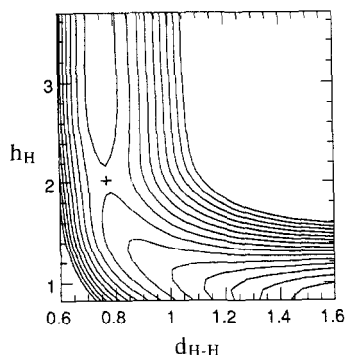


Fig. 2. Potential energy surface for fcc-hcp path.

the transition state, the bond length of the hydrogen molecule is only stretched by 0.04 Å. This transition state is situated in the entrance channel or called an early transition state. The energy barrier along this path is only 71 meV with the zero of the potential corresponding to the state with H<sub>2</sub> far from the surface.

The PES for the bridge-bridge path is presented in Fig. 3. The dissociative adsorption along this path takes place in a very similar way as along the fcc-hcp path. The transition state is located at  $d_{\text{H-H}} = 0.79$  Å and  $h_{\text{H}} = 1.93$  Å. Here, the bond stretching of the hydrogen molecule is nearly the same as in the case of the fcc-hcp path. Again the transition state is situated in the entrance channel. The barrier for this bridge-bridge path is also very small, only 70 meV, i.e. nearly the same as that for the fcc-hcp path.

The two very similar PES's shown in Figs. 4 and 5 are those of the fcc-fcc and hcp-hcp

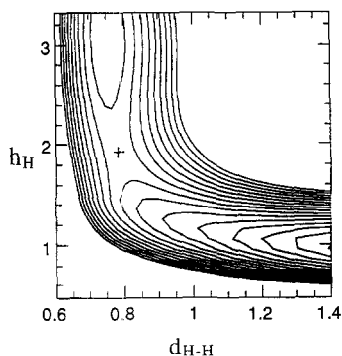


Fig. 3. Potential energy surface for bridge-bridge path.

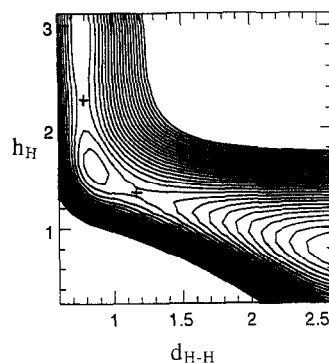


Fig. 4. Potential energy surface for fcc-fcc path.

paths. The remarkable similarity between these two paths can be expected from the similarity between the fcc and hcp sites and that between the end-configurations. The fcc-fcc and hcp-hcp paths are a little more complex than the two paths seen before. Here, the new feature is that a precursor state is found in the constrained space with  $d_{\text{H-H}}$  and  $h_{\text{H}}$  only. Along these two paths, the hydrogen molecule passes a first barrier to reach a precursor state with a physisorbed molecule. The barrier for physisorption is very small, 44 meV and 50 meV for the fcc-fcc and hcp-hcp paths, respectively. At this first transition state, the bond of the hydrogen molecule is not stretched. At the precursor state, there is a gain in energetic stability equal to 138 meV and 124 meV with respect to the nondissociated H<sub>2</sub> far from the surface and a bond stretching of the H<sub>2</sub> molecule of 0.09 Å and 0.08 Å for fcc-fcc and hcp-hcp paths, respectively. The second transition state is situated in

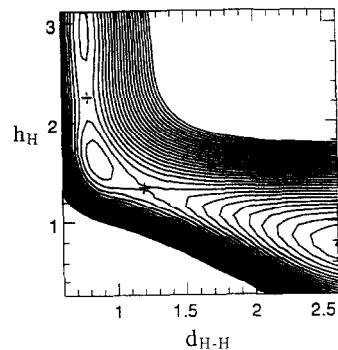


Fig. 5. Potential energy surface for hcp-hcp path.

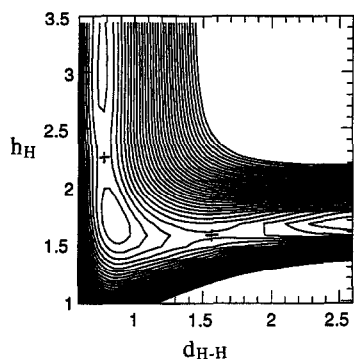


Fig. 6. Potential energy surface for top-top path.

the exit channel (late TS) at strong stretched H–H bonds and the elongations are 0.38 Å (fcc–fcc) and 0.48 Å (hcp–hcp). The barrier heights are 121 meV and 140 meV for the fcc–fcc and hcp–hcp paths, respectively. The barrier height of the second transition state is calculated with the zero of the potential corresponding to the physisorbed molecule. One observes here that larger stretching of the hydrogen molecule bond leads to a higher energy barrier.

The last dissociation path we have examined is the top-top one. Its PES is presented in Fig. 6. This path has a certain similarity to the fcc–fcc and hcp–hcp paths. Some important differences exist also. A precursor state is also found. The first barrier is quite small, only 62 meV. The physisorbed H<sub>2</sub> molecule gains 49 meV in energy compared to the free hydrogen molecule. This energy gain is much smaller than along the fcc–fcc and hcp–hcp paths. At the precursor state, the bond stretching of H<sub>2</sub> is 0.08 Å, a value very close to that found for fcc–fcc and hcp–hcp paths. But the precursor state is located 0.09 Å farther from the surface

than in the cases of fcc–fcc and hcp–hcp paths. This may explain why the energetic gain in this precursor state is smaller. The height of the second barrier is 294 meV. This is the highest barrier in all the cases we have considered. It is directly related to the largest bond stretching of 0.77 Å at the transition state. At this late (exit channel) transition state, the H–H distance is doubled compared to the free H<sub>2</sub> molecule. Finally, all the results for the five dissociative adsorption paths studied in this work are summarized in Table 2 to facilitate the comparisons.

## 5. Conclusions

In the present work, several different paths for the dissociative adsorption of hydrogen molecules on the Pd(111) surface are studied in details by ab initio calculations in the framework of the band theory. For the pathways in which there is small bond stretching, the dissociative adsorption takes place over a low barrier in the entrance channel (or early TS). This is the case for the fcc–hcp and bridge–bridge paths. For the other three paths we have examined, the dissociative adsorption goes through a precursor state. The first barrier to reach the precursor state of a physisorbed molecule is a very low one. However, the second barriers are much higher, ranging from 121 meV to 294 meV, and are all situated in the exit channel (or late TS). The general tendency is that the geometric factor plays a predominant role. Larger bond stretching at the transition state leads to a higher energy barrier. The general tendency we have found here is also perfectly in line with that

Table 2

Dissociation barriers of H<sub>2</sub> on Pd(111) and transition state geometries,  $\theta = (2/3)ML$

Dissociation path	fcc–hcp	Bridge–bridge	fcc–fcc	hcp–hcp	Top–top
$\Delta E$ (eV)	0.071	0.070	0.044 <sup>a</sup> ; 0.121 <sup>b</sup>	0.050 <sup>a</sup> ; 0.140 <sup>b</sup>	0.062 <sup>a</sup> ; 0.294 <sup>b</sup>
$h_H$ (Å)	2.06	1.93	2.30 <sup>a</sup> ; 1.37 <sup>b</sup>	2.27 <sup>a</sup> ; 1.25 <sup>b</sup>	2.24 <sup>a</sup> ; 1.58 <sup>b</sup>
$d_{H-H}$ (Å)	0.78	0.79	0.78 <sup>a</sup> ; 1.12 <sup>b</sup>	0.78 <sup>a</sup> ; 1.22 <sup>b</sup>	0.79 <sup>a</sup> ; 1.53 <sup>b</sup>

<sup>a</sup> First transition state.

<sup>b</sup> Second transition state.

found in the recent work of Kratzer, Hammer, and Norskov on the dissociative adsorption of  $H_2$  on Cu(100) and Cu(111) [55]. The energetically most favorable paths we have found for the dissociative adsorption of  $H_2$  on Pd(111) are the fcc–hcp and bridge–bridge paths. There is only a very small energy barrier equal to 70 meV. This is in fairly good agreement with the estimation, 50 meV, given by Resch et al. [32] based on molecular beam experiments. The existence of a precursor state has been and continues to be a very controversial topic. Although the results given in Figs. 4–6 indicate the possible existence of a precursor state, caution must be taken here. We recall that all the potential energy surfaces presented in this work are determined in a restricted subspace. Further investigations are needed to determine the very existence of the precursor state. Work for this is being undertaken in our group.

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