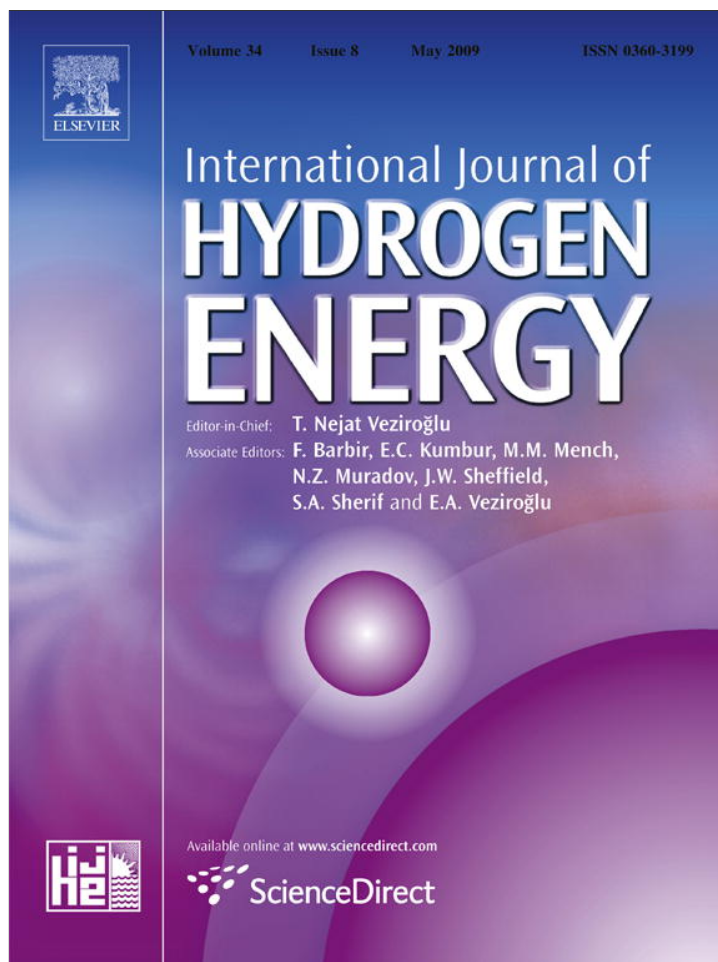


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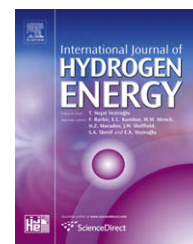


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Simulation of hydrogen trapping at defects in Pd

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ABSTRACT

The interaction of hydrogen with defects in palladium was studied using qualitative electronic structure calculations in the framework of the Atom Superposition and Electron Delocalization Molecular Orbital (ASED-MO) theory. Interatomic distances, energies and electronic structure for hydrogen at a dislocation and at a vacancy were determined and compared with that for an octahedral site in the Pd fcc lattice. We found that a repulsive H–H interaction is developed if these atoms occupy interstitial sites in a regular lattice. However, when the H atoms are close to a dislocation, the accumulation becomes possible. It was found that the dislocation allows hydrogen association at interatomic distances close to molecular hydrogen. The Density of States (DOS) and Crystal Orbital Overlap Population (COOP) curves were used to shed more light on the interstitial-Pd-defect interactions. Hydrogen produce changes in the local and global electronic structure of the host metal and induce changes in the cohesive forces between atoms in the host matrix. In all cases, it was found that strong bonds between Pd and H atoms are formed while metal–metal bonds are weakened. The metal–hydrogen bonds were characterized by charge transfer from metal atoms to hydrogen.

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1. Introduction

Hydrogen–metal systems have been widely studied and investigated by scientists and engineers. This has been motivated by the technological importance of hydrogen storage as fuel for the future as well as the effects of absorbed hydrogen on material properties [1].

The diffusion of hydrogen and hydrogen isotopes in metals has been an active area of research for decades. The diffusivities of hydrogen, deuterium, and, to a lesser extent, tritium in several metals and alloys have been characterized under a variety of conditions and using several techniques. Beyond these basic studies, the effect of defect interactions, such as those associated with grain boundaries and dislocations on the H diffusion has been a subject of major interest [2].

The characterization of the interaction of hydrogen with defects in palladium offers potential to obtain information

about interstitial H-defect interactions. In well-annealed palladium, the initial dilute phase hydrogen solubility obeys Sieverts law. Deviations from this behavior must be due to the presence of defects [3]. For example, the presence of dislocations, when they are present in densities of $\geq 10^{14} \text{ m}^{-2}$, causes an enhanced solubility [4–7]. The types of defects that should be considered as having the potential to affect hydrogen solubility are those that can be introduced into any metal, e.g. point defects such as vacancies and impurity atoms, and extended defects such as dislocations, grain boundaries, and external surfaces [3]. Dislocations are always present in materials because they are introduced during processing such as during rolling or grinding, or as the result of thermal stresses that appears during the solidification of the melt [8].

Hydrogen and deuterium interactions in palladium were studied by different theoretical methods. Sun and Tománek [9], using an *ab-initio* density-functional calculation, found

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that even at very high D concentrations in the bulk, the equilibrium distance between two D atoms is increased by $\approx 0.2 \text{ \AA}$ from the gas value. Hydrogen interactions in PdH_n ($1 \leq n \leq 4$) were studied by Wang et al. [10] using a first-principles pseudopotential total-energy approach. They found that the separation between H atoms remains much larger than the value required for a significant fusion rate. *ab-initio* computations of one and two H or D atoms in Pd tetrahedral site was studied by Muguet and Bassez [11] and their results show that the tetrahedral site does not favor a closer deuteron encounter. No metastable dimer geometry was found. The two deuterons repel each other despite the screening. The influence of electronic structure on H absorption in Pd alloys was investigated by Ke et al. [12,13]. They found that more stable H absorption is correlated with the H 1s electrons, Pd s electrons, Pd s-like electrons and Pd d electrons moving higher in energy towards the Fermi level. The interaction between interstitial hydrogen and alloying atoms in palladium were calculated by first-principles by Li et al. [14]. The calculation results show that almost all the considered alloying atoms are repulsive to hydrogen. Interstitial solute trapping by edge dislocations was studied by Wolfer and Baskes [15]. In this case, the Fermi-Dirac statistic is used to account for the short-range repulsive interactions which prevent dual site occupancy. The enhancement of H solubility in Pd due to trapping in the strain field of edge dislocations was evaluated and compared with experimental results.

The hydrogen-dislocations interactions in palladium have been experimentally studied [16]. Nechaev [17] found that the formation of hydride-like segregation phases at dislocations occurs at high degrees of undersaturation on the solid solutions with respect to the hydride precipitation in the normal lattice of Pd. This means that a specific phase diagram can be considered for a “H-near-dislocation segregation Pd nanoregions” systems in comparison with the conventional hydrogen–palladium phase diagram. Votyakov et al. [18] found that the dissolution of H in Pd changes the properties of the metal and can result in its hydrogen embrittlement and cracking, which depends on the motion parameters of dislocations.

In this paper, we present a semi-empirical molecular orbital study to explore the H interactions in Pd including a dislocation under conditions of high H concentrations. To model the trapping of hydrogen at defects in Pd fcc we used the Atom Superposition and Electronic Delocalization (ASED) method. The details of our calculations can be found in Section 3. As a comparison, we also present the results of hydrogen at octahedral site in a normal fcc Pd lattice.

2. The Pd dislocation model

For some metals there is a structural phase transformation of the metal lattice in passing from the α to the β phase. In the case of palladium, there is only a change in the lattice constant of the fcc lattice. Palladium hydride may be considered an interstitial alloy, PdH_x , $0 \leq x \leq 1$, where octahedral sites of the fcc metal lattice are occupied by hydrogen [19,20]. In dilute phase, the square root dependence on pressure proves that H_2 dissociates upon entering the Pd lattice [5,21]. However, as all the octahedral interstitials are progressively filled by hydrogen,

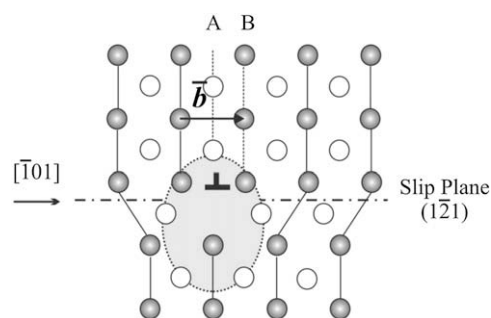


Fig. 1 – Atomic structure of the Pd $(\bar{1}21)[\bar{1}01]$ dislocation. It contains two alternating planes shown with grey and white circles. \bar{b} is the Burgers vector, $b = 2.75 \text{ \AA}$. The core zone is also shown.

a “spill-over” occurs as hydrogen occupies the next higher energy tetrahedral interstitials, driven by a higher molecular fugacity, which is in turn governed by higher gas pressure [22].

The palladium lattice parameter is 3.89 \AA (298 K). Upon hydrogen absorption the lattice undergoes an isotropic expansion while retaining its fcc structure. In the dilute α -phase, at 298 K, the lattice parameter of PdH_α is 3.894 \AA ($\text{H}/\text{Pd} \approx 0.015$) [3]. We used a lattice parameter of 3.89 \AA for our calculations.

To generate the edge dislocation, we started stacking $(\bar{1}21)$ planes of the fcc regular structure. Then, two neighboring half planes of atoms (A and B of Fig. 1) were inserted into the lattice. The place where the half planes terminate is the dislocation line. The Burgers vector, \bar{b} , with $[\bar{1}01]$ direction and module $b = 2.75 \text{ \AA}$ is perpendicular to the dislocation line. Such a dislocation gives rise to an elastic distortion of the lattice around the line of the defect, and consequently to a stress field with which solute impurities may interact. In Fig. 1, we can see that the atomic structure of the dislocation core is that of a cylinder-shaped region sitting immediately below the dislocation line, with bigger interatomic distances than in a perfect lattice. We used a cluster of 102 Pd atoms to perform our calculations. Recently, we used the same cluster approach to model several defects such as dislocation [23], vacancies [24,25], grain boundaries [26] and stacking faults [27,28], being this representation useful to study local effects during interactions with point and line defects. The same approach was also used successfully by Crespo et al. [29] to model H absorption on Pd and Ni.

3. Computational method

The calculations were carried out using the atom superposition and electron delocalization molecular orbital cluster method (ASED-MO) [30]. The ASED-MO is a semi-empirical method, which makes a reasonable prediction of molecular and electronic structures. This theory is based on a physical model of molecular and solid electronic charge density distribution functions, where by the latter it is partitioned into a perfect following (with respect to the nucleus) atom part and an imperfect following bond charge part [30,31]. This method was described in a previous paper [32].

Table 1 – Interatomic distances and energies for H–Pd in a perfect lattice (O-site) and near the dislocation core.

H	Distance [Å]		ΔE [eV]
	Pd–H	H–H	
O-site			
1	1.60	–	–5.14
2	1.57	2.23	–4.36
Dislocation			
1	1.64	–	–5.27
2	1.64	3.90	–4.65
3	1.57	2.46	–4.43
4	1.75	2.62	–4.41
5	1.57	2.46	–4.37
6	1.62	2.45	–4.28
7	1.76	2.68	–4.31
8	1.49	2.03	–3.92
9	1.74	0.82	–3.50
10	1.87	0.76	–3.42

Table 2 – Electron densities and net charges for a perfect crystal clusters and for the dislocation, without and with H atoms.^a

Structure	Electron density			Charge
	<i>s</i>	<i>p</i>	<i>d</i>	
O-site				
Pd				
Pd _{bulk}	0.584	0.310	8.533	0.573
Pd–H				
Pd*	0.518	0.334	8.413	0.735
H1	1.161	–	–	–0.161
Pd–2H				
Pd*	0.520	0.335	8.391	0.754
Pd**	0.494	0.320	8.451	0.736
H1	1.150	–	–	–0.150
H2	1.146	–	–	–0.146
Dislocation				
Pd				
Pd _{II}	0.592	0.289	8.518	0.601
Pd–H				
Pd _{II}	0.529	0.338	8.341	0.792
H1	1.203	–	–	–0.203
Pd–2H				
Pd _{II}	0.529	0.338	8.343	0.790
Pd _{IV}	0.529	0.338	8.343	0.790
H1	1.203	–	–	–0.203
H2	1.203	–	–	–0.203
Pd–10H				
Pd _{III}	0.372	0.274	8.447	0.907
Pd _{IV}	0.424	0.285	8.517	0.774
H1	1.186	–	–	–0.186
H2	0.946	–	–	0.054
H10	0.885	–	–	0.115

^a The Pd and H identification can be seen as the insert in Table 3. * and ** identify the first neighbor to H1 and to H2, respectively.

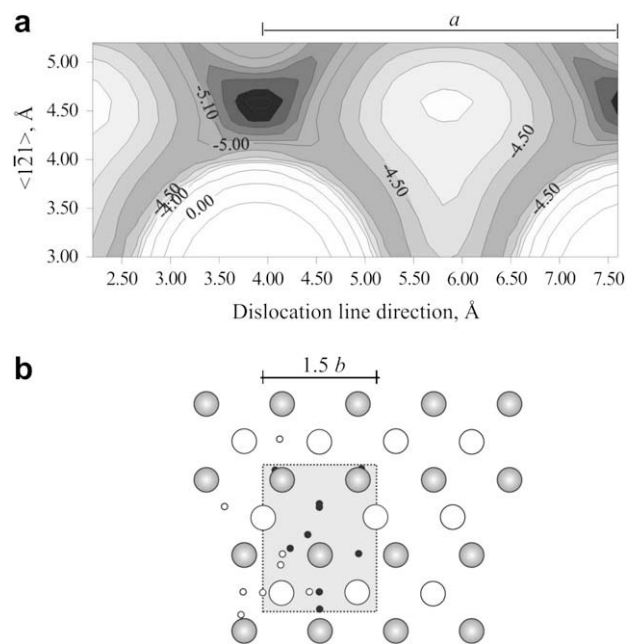


Fig. 2 – (a) Contour energies lines in the core of a dislocation, with one H. $E_{\min} = -5.27$ eV. (b) Dislocation view parallel to the dislocation line. White and grey big circles represent not equivalent $\langle 1\bar{2}1 \rangle$ planes. Black and white small circles represent H atoms inside and outside the select zone, respectively.

The total-energy difference can be expressed as:

$$\Delta E_{\text{total}} = E(\text{Pd}_m\text{H}_n) - E(\text{Pd}_m\text{H}_{n-1}) - E(\text{H}) + \sum E_{\text{repulsion}}, \quad n \geq 1$$

where E is the electronic energy, m is the cluster size and n is the number of H atoms. The repulsion energy ($E_{\text{repulsion}}$) of nucleus B in the presence of a fixed atom A is calculated from:

$$E_{\text{repulsion}} = \frac{1}{2} \sum_A \sum_{B \neq A} E_{AB}$$

where E_{AB} is a pairwise electrostatic energy term. The summation is extended over all Pd–Pd, Pd–H and H–H pairs [30]. The parameters were taken from [33].

Throughout this paper, two conceptual tools: density of states (DOS) and crystal orbital overlap population (COOP) curves were used to shed more light on the Pd–H interactions computed with the YAHEMOP program [34]. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighed DOS vs. energy. Integration of the COOP curve up to the E_F gives the total overlap population of the bond specified. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms or orbitals [35].

4. Results and discussion

We have studied the location of H and the changes in the electronic structure when this impurity is in the bulk, at a dislocation and near a vacancy.

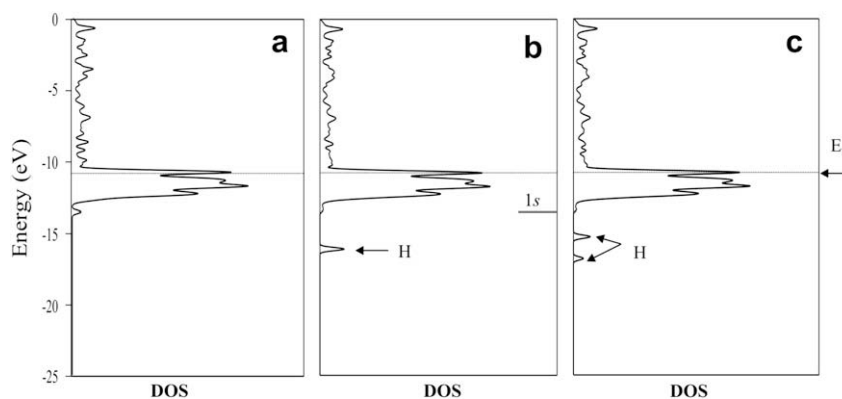


Fig. 3 – Contribution to DOS for the Pd atom of the octahedral site, first neighbor to H1 in: a) Pd, b) Pd-H and c) Pd-2H clusters. The bar on the left in (b) is the H state before absorption.

4.1. H location

4.1.1. The bulk

First of all, we have performed calculations for an H atom inside a perfect crystal to find the most stable localization for an interstitial H. Metal atoms first neighbor to the interstitial were relaxed while maintaining the rest fixed. The location of the extra H atom was varied at 0.01 Å steps and then the geometry of the system was relaxed again. We have calculated the energy for the H atom located in different positions of the (010) plane that contain an octahedral site (O). We can see that the H atom achieves the higher stability out of center of this site. Then, we performed calculations with the H on a plane that contains this relative minimum, perpendicular to the first, and so on until we reach the minimum energy, this is -5.14 eV for an O-site (see Table 1). This preference for O-site in Pd fcc was also reported in Ref. [12]. Recent theoretical studies have predicted that subsurface hydrogen will preferentially occupy the octahedral interstitial sites over the tetrahedral interstitial sites [36–38].

Our results show that when the H is at O-site, there is charge transference from Pd to H of 0.161 (see Table 2). Paul and Sautet [38] have shown theoretically that charge transfer occurs between hydrogen in the subsurface sites and the surface Pd atoms that become more positively charged and the subsurface hydrogen atoms that become negatively charged.

After that, while the first H atom is located in its energetic minimum, a second H atom was situated on different sites of distinct planes, always at the O-site, and the energy for this system was computed. This energy minimum is -4.36 eV. We have also found that the H-H pair is located on the $\langle 111 \rangle$ direction. This result agrees with previous *ab-initio* calculations [39–41]. The H-H separation (2.23 Å) greatly exceeds that for the H₂ molecule in the ground state.

In summary, we have found that the H-H interaction is more repulsive inside Pd fcc than for free H₂ molecule calculated with the same theoretical method (computed H-H distance in gas phase: 0.76 Å, with an energy of -9.38 eV).

Our results for binding energy of hydrogen in ideal Pd does not agree with the experiment because AS-E-D-MO calculations overestimate the absolute values for energies, so we will discuss the trends in the change of the electronic characteristics.

4.1.2. H at a dislocation

To find the most stable localization for the H atom within the dislocation, we have performed calculation with the H located in different positions of a surface perpendicular to the slip plane that contain the dislocation line. Fig. 2(a) shows contour lines for the total energy, with a minimum of -5.27 eV. We have confirmed this value computing the energies in other planes, perpendicular to the first. In Fig. 2(a) we can see that the sites with minimum energy are separated by a lattice constant.

For the additional H atoms, we select a zone with a volume of $(a \times 2a \times 1.5b)$ containing the dislocation core, being a the lattice parameter and b the Burgers vector module (see Fig. 2 (b)). Later, with the first H atom residing at the most stable position we have computed the energy for a second H, a third H, and similarly up to 10 H. When the tenth H is considered an H-H distance close to 0.76 Å, it can be detected. The experimental bond distance for Pd-H in the stable palladium hydride is 1.53 Å [42]. Our calculated results for Pd-H distances are presented in Table 1, varying from 1.57 to 1.87 Å. The locations for the H inside the selected zone are represented by black circles in Fig. 2(b) and the H-H distance range is 0.76–3.90 Å.

Heuser et al. [1,43,44] have found that the number of hydrogen atoms in the bulk of the sample is negligible compared with the number of hydrogen atoms at the dislocation. At room temperature, about 30% of the total hydrogen concentration goes to the dislocation. Small-angle neutron scattering (SANS) measurements have shown that, on average, 2–5 hydrogen atoms are trapped per Å of dislocation line and they found that the majority of trapped deuterons lie within a few Burgers vectors of the dislocation core. We must note that the radius of the hydrogen-enriched cylindrical region formed below the dislocation line of an edge dislocation continuously grows with the total hydrogen concentration in the solid solution [8]. Our results are 2.6 H atoms per Å of dislocation line (10/3.89 H/Å).

A characteristic parameter of the trapping is the “trap binding energy” which is the energy of the H atom on the defect relative to its energy on a normal interstitial site (in this case, an O-site). In the case of our dislocation, the binding energy result be 0.13 eV. Heuser and King [43] report a binding energy of 0.20 eV to characterize the trapping interaction in both cold-rolled and hydride cycled Pd.

Table 3 – Interatomic distances and OPs for Pd bulk, for an octahedral site and a dislocation core.

Structure	Bond	Distance [Å]	OP	
Pd _(bulk)	Pd–Pd	2.75	0.129	
	O-site			
	Pd–H	Pd–Pd*	2.75	0.071
		H1–Pd*	1.60	0.273
	Pd–2H	Pd–Pd*	2.75	0.072
		H1–Pd*	1.60	0.282
H2–Pd**		1.57	0.281	
H1–H2		2.23	0.011	
Dislocation				
Pd	Pd _I –Pd _{II}	2.75	0.148	
	Pd _{II} –Pd _{IV}	3.89	0.000	
	Pd _{III} –Pd _{IV}	2.75	0.148	
Pd–H	H1–Pd _{II}	1.64	0.303	
	Pd _I –Pd _{II}	2.75	0.088	
	Pd _{II} –Pd _{IV}	3.89	0.000	
Pd–2H	H1–H2	3.90	0.000	
	H2–Pd _{IV}	1.64	0.303	
	H1–Pd _{II}	1.64	0.303	
	Pd _{III} –Pd _{IV}	2.75	0.088	
Pd–10H	H2–H10	0.76	0.628	
	H2–Pd _{IV}	1.64	0.128	
	H10–Pd _{III}	1.87	0.062	
	Pd _{III} –Pd _{IV}	2.75	0.059	
	(a) Identification for the atoms of the octahedral site. 1 and 2 represent the first and the second H at the O-site. * and ** identify the first neighbor to H1 and H2, respectively. (b) Identification for the atoms of the dislocation. White and grey big circles represent not equivalent {121} planes. Black and white small circles represent H atoms inside and outside of the select zone, respectively.			

4.1.3. H near a vacancy

We have also performed calculations for a single H occupation of a Pd vacancy model. We have used a cluster with the same number of palladium atoms than in the dislocation model. We found that the regions of higher stability are off center in good agreement to Schober et al. [45] who explains that the H atoms are displaced towards the faces of the vacancy to locations of optimum electron density.

We have found that the Pd–H distance is similar to that for the first H at the dislocation core, although the size of the hollow is different ($d_{\text{Pd-H}} = 1.66 \text{ \AA}$, $E = -5.16 \text{ eV}$).

4.2. Electronic structure

4.2.1. H at the O-site in fcc Pd

Fig. 3 shows the projected density of states (DOS) curve for a Pd atom next to the octahedral site which is the more stable location for H in a normal fcc Pd lattice. The metals' *d*-states

form a narrow band between -10.4 and -12.8 eV and the *s* and *p*-states, on the other hand, are more dispersed. When one H atom is located in the O-site, the projected DOS curve also presents a small peak located at -16.12 eV indicating the interaction between H and its first neighbor. In the projected DOS curve for the same Pd atom in the cluster with two H atoms we can see a similar *d*-band and two narrow bands at -15.29 and -16.81 eV corresponding to the contribution of the H atoms. Regarding the bonding, the more stable interaction includes H 1s electrons and Pd *s* electrons. The H population changes 16% while the Pd 5s changes 11% and Pd 5p only 7%. This result is similar to that reported by [12]. The *s*, *p* and *d* electron densities and charge are shown in Table 2.

The overlap population (OP) for different pairs of atoms could be considered as a measure of the bond strength. Table 3 shows the interatomic distances between some atoms of the octahedral site and the corresponding OP values. When an H is placed at this site some Pd–H bonds are formed while Pd–Pd bonds next to the H are weakened (about 45%). The effect of one or two H on the neighbor Pd of the O-site is similar. Because of the repulsive interaction between H atoms, H–H pair presents a very weak bonding interaction.

4.2.2. H at the dislocation

We have identified the atoms for the dislocation in Table 3. In Fig. 4 (a), crystal orbital overlap population (COOP) curves are plotted for a cluster of clean dislocated Pd for two Pd pairs next to the dislocation. Pd_I–Pd_{II} has interatomic distance very different to Pd_{II}–Pd_{IV} (3.89 Å vs. 2.75 Å, as show in Table 3). There are more Pd–Pd bonding states occupied by atoms like those perpendicular to the dislocation line than the parallel one, and this bond is 15% higher than the Pd–Pd bulk value (0.148 vs. 0.129) at the same interatomic distance (see Table 3 for the bulk).

When an H is placed at the dislocation, a new bonding state arises principally from the interaction between the H 1s and Pd 5s orbitals. A similar result was obtained using *ab-initio* calculations [12]. Fig. 4 (b) compares the projected DOS for Pd_{II} in the clean dislocation and with an H atom. It can be seen that the DOS has a peak below -15 eV which is mainly H 1s stabilized by the H–Pd interactions. There is a charge transfer from Pd to H (see Table 2). As shown from the COOP curves in Fig. 4(c), an H–Pd bond is achieved at the expense of weakening Pd–Pd bond (about 40%). The Pd–H interaction is 10% stronger for the H atom bond to Pd at the dislocation than at the octahedral site (0.303 vs. 0.273).

The second H atom that is located at the dislocation core achieves the most favorable position far away from the first H (3.90 Å) and the effect on the first neighbor Pd atom is similar (see the charge values and OPs in Tables 2 and 3).

When 10 H are added to the Pd dislocation, the DOS in Fig. 5 (a) shows several peaks between -15 and -20 eV . These peaks are mainly due to Pd–H interactions within the Pd matrix. The results in Table 3 show that the Pd–Pd bonds first neighbors to the H are more weakened than when only one H is at the dislocation (Pd–Pd OP: 0.059 vs. 0.088). Due to the presence of H the metal bond strength decreases 60% compared to the clean Pd. The effect of the additional H is similar to the first H with a greater extent. After considering ten hydrogen; the final H–H interaction is strong (OP: 0.628) when compared to that at the O-site (OP: 0.011). Under the

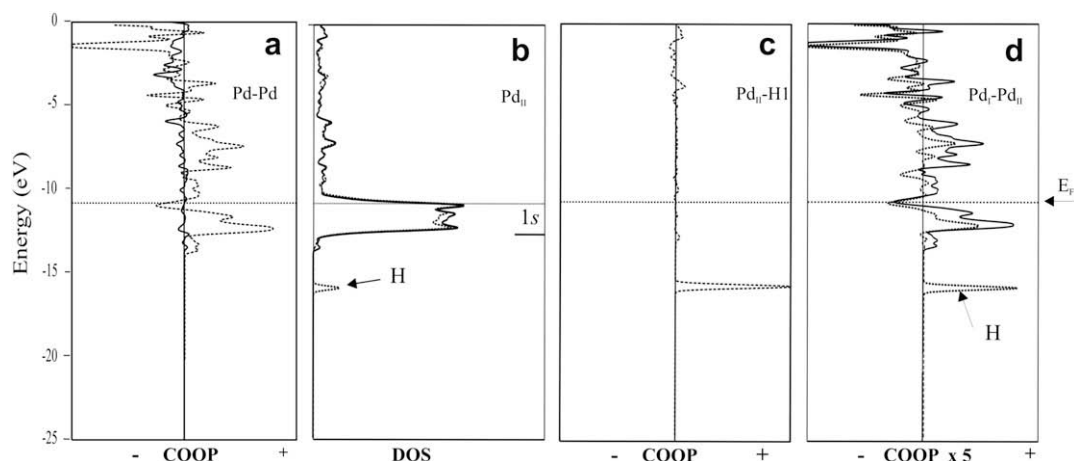


Fig. 4 – Electronic structure of the dislocation. (a) Without H: COOP curves for Pd_I–Pd_{II} (dashed line) and for Pd_{II}–Pd_{IV} (solid line). (b–d): With an H atom and for the clean Pd (dashed and solid line, respectively). Pd_{II} is on the surface of the dislocation void and H1 is the first neighbor to Pd_{II}.

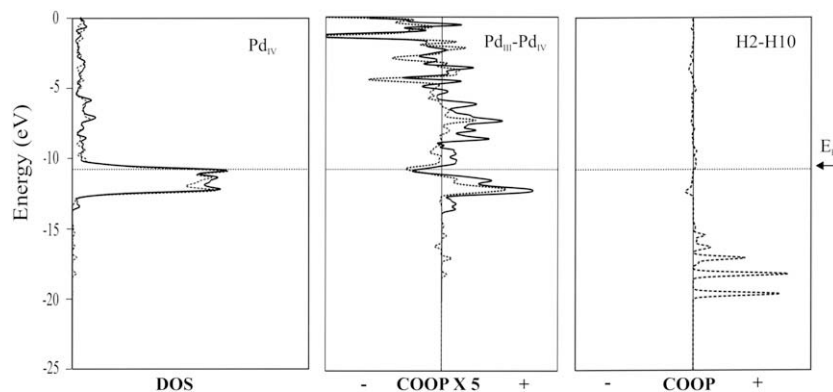


Fig. 5 – Electronic structure of the dislocation with 10 H (dashed line) and without H (solid line).

ASED approximation, the OP for the H₂ molecule at the equilibrium distance (0.78 Å) is 0.845.

5. Conclusions

We have studied the electronic structure and energetics of hydrogen atoms at palladium metal models. We have shown that in some defects like dislocations, the formation of an H–H associated state is energetically possible. It is remarkable that local minima in the total energies are located at similar values of Pd–H distances irrespective of the adsorption site. Similar results were found by Watari et al. [46] for H in Pd clusters using a self consistent density-functional method. The total energy of the system with an H atom at octahedral site or at a dislocation core is similar with a binding energy of 0.13 eV. The differences are mainly the amount of H that can be accumulated in each configuration. When an H pair is at octahedral site, the dimer lies along the <111> direction. For the structures of lowest energy, the H–H separation is bigger than that of gas phase H₂ molecule, although when the H pair

is at a dislocation, it is possible to reach a similar distance, at a higher energy. The total calculated amount of hydrogen trapped at dislocations is 2.6 atoms per Å of dislocation line, which could be larger depending on the core size.

Physical properties of systems with dominant contributions of micro structural defects can be quite different from those of the bulk. Besides bringing changes in local and global electronic structure of the host metal, hydrogen also induces changes in the cohesive forces between atoms in the host matrix. The charge transfer from the electron-rich metal atom to H is responsible for the strong metal–hydrogen bond and is an impediment to the formation of molecular hydrogen in a metal lattice. This conclusion is in agreement with *ab-initio* calculations from other authors [47].

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