Ab-Initio Determination of Palladium Hydride Properties and Application to Hydrogen Storage

Khalida Bennouna[1], Louiza Zenkhri[1*], Boudjema Souheyla[2,3], Aomar Boukraa[4], Mohammed Lakhdar Belfar[1]

[1] Laboratory of Valorization and Promotion of Saharan Resources (VPRS), Chemistry Department, University Kasdi Merbah – Ouargla, 30000, Ouargla, Algeria

[2] Oil Drilling and Mechanics Department, Kasdi Merbah University, BP 511 Route Ghardaia, Ouargla, Algeria

[3] Laboratory of Catalysis and Synthesis in Organic Chemistry, Tlemcen University, BP 119, Imama, Tlemcen, Algeria.

[4] Laboratory of New and Renewable Energy in Aride Zones (LENREZA), Physics Department, University Kasdi Merbah – Ouargla, 30000, Ouargla, Algeria

Email : louizazenkhri@yahoo.fr

ABSTRACT

In this work, we presented a theoretical study on the structural and electronic properties of palladium hydride and demonstrated the usefulness of modelling by choosing the most appropriate hydride to find the possibility of storing hydrogen as a new energy in the palladium. Thus, the structural and electronic properties of pure palladium were compared with those of palladium hydrides PdH_x (x = 0.25, 0.50, 0.75, 1) using the ab-initio method known as the linear augmented plane wave method (FP-LAPW) based on density functional theory calculations, implemented in the Wien2k code. The results obtained for band structure and state density have been improved to previous theoretical work and showed that hydrogen absorption is accompanied by a significant dilation of the crystalline lattice. The PdH_x hydride possesses metallic properties, and both total and partial DOS calculations show that the palladium 3d and hydrogen 1s states exhibit the greatest hybridization. In the palladium hydrides studied PdH_x, the electrons decrease their energy leading to a large binding force between Pd and H atoms which leads to a more stable system.

KEYWORDS : Ab-initio, WIEN2K, Hydride, DFT, hydrogen storag.

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1. Introduction

Hydrogen is a substitute for traditional fossil fuels that has a lower cost and less negative impact on the environment [1]. Hydrogen as energy is lately used in several applications such as fuel cell applications [2], sensors [3]… Palladium is a metal of choice for numerous applications, including electrodes in fuel cells, due to its ability to trap a significant amount of hydrogen. So recently, systems with a palladium and hydride balance have been designed for the storage of hydrogen. Palladium (Pd) exhibits a number of remarkable qualities that make it possible for it to be used in a wide variety of hydrogen-based processes. He is a good catalyst that is frequently used in hydrogenation and dehydrogenation reactions [4]. It can be identified by a strong propensity for sorbing hydrogen in the gas phase [5] at room temperature and atmospheric pressure, and then forms palladium hydride (PdH_x) [6]. It is necessary for many industrial applications due to its chemical and physical properties. It is utilized in environmentally beneficial applications, particularly in automobile sector catalysts. Its market is really modest, nevertheless. Although Pd is known to have a low storage capacity, it is used as a hydrogen sponge because of its ability to store hydrogen under ambient conditions. Several studies have been carried out to improve Pd's reversible hydrogen storage capacity [7].

Due to hydrogen's lighter weight and ease of movement between octahedral and tetrahedral sites, we cannot locate all of the palladium's octahedral sites occupied in nature. $PdH_{0.75}$ may occur, but $PdH_{0.25}$ and $PdH_{0.50}$ are only studied theoretically. In this study, we investigated the structural, thermodynamic, and electronic characteristics of Pd, PdH, and the hydrides $PdH_{0.25}$, $PdH_{0.50}$, and $PdH_{0.75}$, respectively, using three, two, and one vacant octahedral site.

2. Materials and Methods

The calculations are performed with the aid of the ab initio electronic structure calculation code WIEN2K [8], which implements the FP-(L)APW+lo technique within the DFT [9] framework to perform electron structure calculations of solids. Our estimates were semi-relativistic. (The spin-orbit effect is neglected). The local density estimate (LDA) set up by Perdew and Wang [10] has been used in order to characterize the exchange and correlation potential. The structural properties at static equilibrium such as the parameter of the a_0 network, the compressibility module B_0 (bulkmodulus) and its derivative in relation to the pressure B'_0 were detérminé by the total energy calculation E(V) for different values of the volume of the primitive cell, then adjusted the points E(V) calculated by the Murnaghan state equation [11] given by the formula:

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left|\frac{\left(\frac{V_0}{V}\right)^{E_0}}{B_0' + 1}\right| - \frac{B_0 V_0}{B_0' - 1}$$

Parameter values that affect the time and accuracy of the calculation have been specified and the Muffin-tin ray (R_{MT}) values we used for Pd and PdH are a good choice for our calculation. This

decision was based on two criteria: to guarantee that the majority of the core electrons are integrated in the sphere (Muffin-tin) and to avoid overlapping spheres (Muffin-tin). The cut-off parameter R_{MTmin} K , R_{MTmin} is the smallest radius of the sphere MT and K_{max} the standard of the largest wave vector used for the development in plane waves of the own functions. The number of k-points considered in the irreducible area of Brillouin.

The total energy E_{tot} of the Pd and PdH compounds were tested for convergence as a function of the R_{MTmin} and K_{max} cutoff values and specifically for PdH, as a function of the number of k-points in the reduced Brillouin area. The tetrahedron method [12, 13] is used to determine the state density of these compounds witch needs a lot of points in the Brillouin region.

Convergence tests of the total energy E_{tot} for Pd and PdH compounds as a function of the R_{MTmin} K_{max} cutoff parameters and as a function of the number of k-points in the reduced Brillouin area for PdH only were performed. All the parameters used for the calculations carried out on the two compounds Pd and PdH are gathered in Table 1. The states Pd ($4d^{10}$ $5s^{0}$) and H ($1s^{1}$) were chosen as valence states.

Table 1: The various parameters included in the calculation for PdH_x (0, 0.25, 0.50, 0.75, 1)

composé	R_{MT}	$R_{MT_{min}} * K_{max}$	Number of k-points in PZB and Special points in Brillouin's irreducible zone	l_{max}	G_{max}
Pd	Pd(2.56) Pd(2.5)H(1.1)	7	600 (72 pts special)	10	12
$PdH_{0.25}$	Pd(2.58)H(1.16)	4	600(145 pts special)		20
$PdH_{0.50}$					
$PdH_{0.75}$	Pd(2.5)H(1.28)	4	600		20
PdH	Pd(2.5)H(1.23)	4	600		20
	Pd(2.599)H(1.399)[14]	4	600		20

3. Results and Discussion

Palladium metal cristallize in face centered cubic (fcc) structure. This structure contains different faces for palladium metal crystal : (1 1 0), (1 0 0), (1 1 1) plane. (1 1 1) is the most densely packed [15] [16]. In the hydrogen palladium system, hydrogen atoms occupy the octahedral interstitial sites of the fcc metal sub-network as shown in fig. 1.

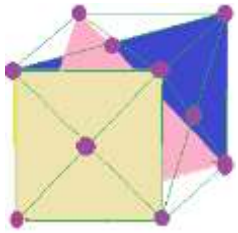


Fig. 1. Palladium unit cell showing (1 1 1) plane (pink), (1 0 0) plane (yellow) and (1 1 0) plane (blue);

3.1. Convergence test

In order to obtain the correct values of $R_{MTmin} * K_{max}$ and the number of k-points ensuring the convergence of the system total energy with more precision, the value of k-points equal to 100 was set and the values of $R_{MTmin} * K_{max}$ were varied, for each of these values, the total energy for each material was calculated and curves were plotted according to figure 2 and 3.

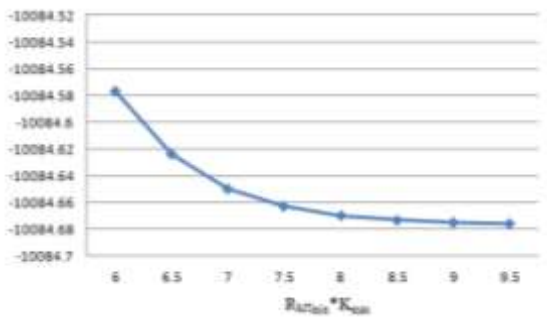


Fig. 2. Change in total energy as a function of values of $RMT_{min} * K_{max}$ pour le Pd

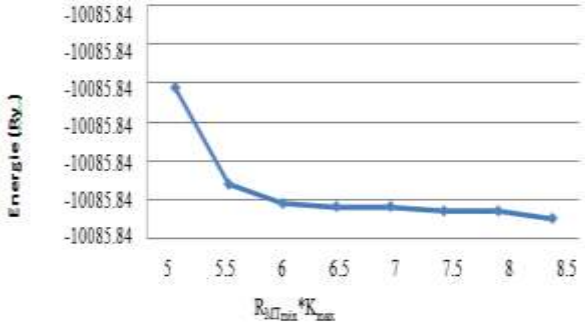


Fig. 3. Change in total energy as a function of values of $R_{Mtmin} * K_{max}$ pour le pdH

After the determination of $RMT_{min} * K_{max}$ values, the latter was set to the converging value and the number of points k in the PZB was varied, for each of these values the total energy of each compound was calculated and the curve was drawn (Figure 4).

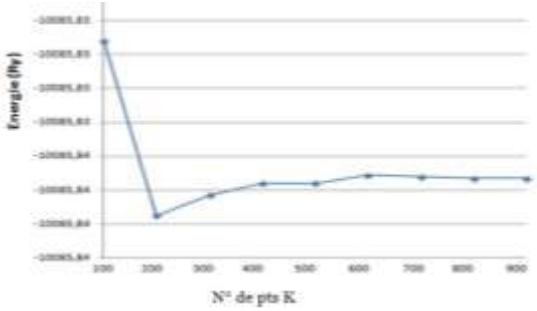


Fig. 4. Change in total energy as a function of the number of K points for le PdH

3.2. Calculation of structural parameters

Figure 5 shows the change in optimized total energy as a function of the volume of the Pd element and $PdH_{0.25}$, $PdH_{0.50}$, $PdH_{0.75}$ and PdH compounds.

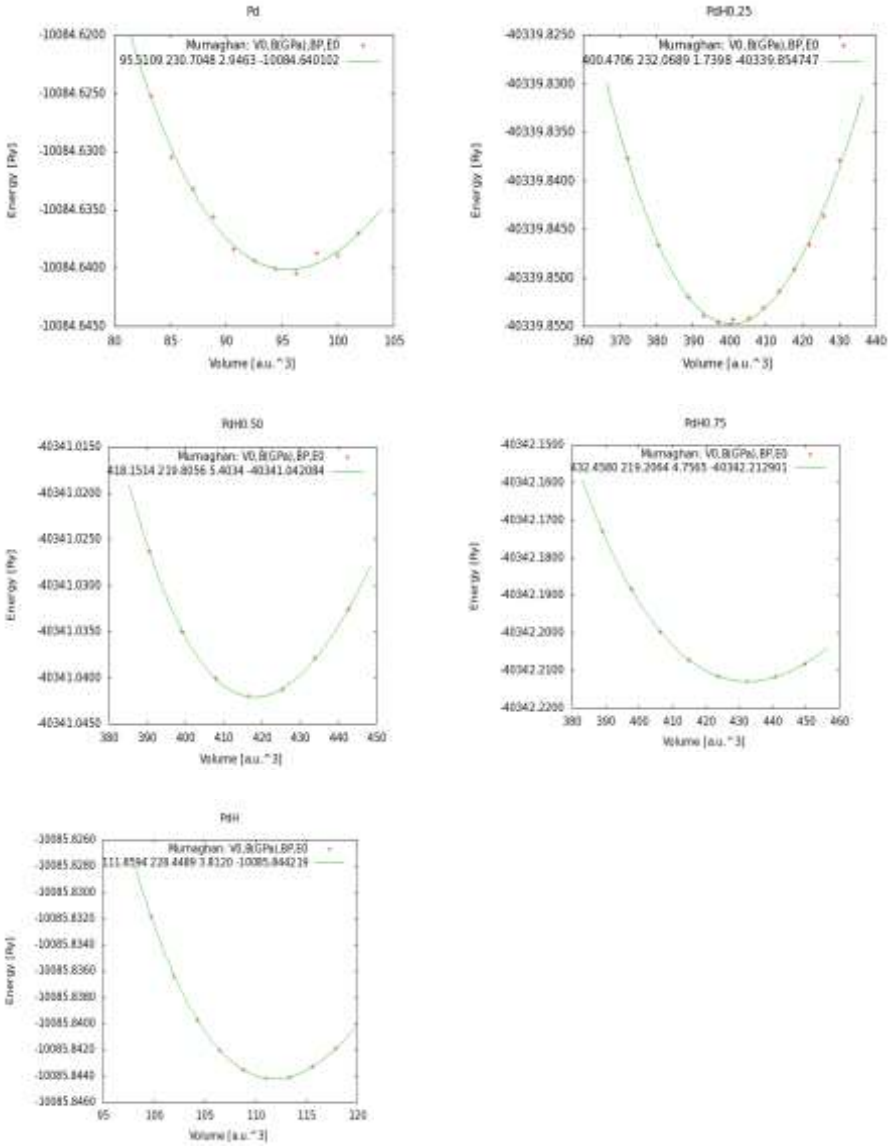


Fig. 5. Volume optimization of Pd and PdH_x systems (x = 0.25, 0.50, 0.75, 1)

Table 2 gathers results of structural parameters of the compounds fundamental state (lattice parameters and compression modules) calculated by ab-initio method using the LDA. Experimental values were also included in the table when available for ease of comparison.

Table 2: Results of LDA calculations of structural parameters of the fundamental state for the compounds under study as well as research findings.

PdH_x	a_0(Å)	B_0(GPa)	B_0'(GPa)
Pd	3.8457423*, 3.8960 [17] ,3.8796 [18], 3.88 [19]	234.9077*, 230.8 [22],	2.9463*
$PdH_{0.25}$	3.90663*, 3.94 [20]	232.0689*	1.7398*
$PdH_{0.50}$	3.963234*	219 .8056*	5.4034*
$PdH_{0.75}$	4.007966*	219.2064*	4.7565*
PdH	4.053716399*, 4.03 [21], 4.09637 [17], 4.07 [20]	228.4489*, 224.5[14], 223.8[21], 225.5[23].	3.8120*

*: this work .

The results given in Table 2 show that hydrogen absorption is accompanied by significant expansion in crystalline networks, and these results are in good agreement with the experimental results reported in the literature. The values of the optimized energies are presented in Table 3.

3.3 Thermodynamic properties

The absorption step for formation of metal hydrides depends on molecular dissociation H_2. Dissociative adsorption of H_2 occurs with activation energy barrier on palladium surfaces. Dehydrogenation of palladium occurs by the following reaction:

$$PdH_x \rightleftarrows Pd + x/2\, H_2$$

Then the training enthalpy will be:

$$\Delta H_{formation} = E_{tot}(PdH_x) - E_{tot}(Pd) - x/2\, E_{tot}(H_2)$$

Table 3 shows energies of PdH_x hydrides (x = 0.25, 0.50, 0.75) and Enthalpie of formation optimised in the calculations for minima using FP-LAPW. H_2 energy value calculated for a free molecule under the same conditions is: E_{H2} = -2.17006 R_y . Knowing that the calculated palladium energy is equal to: -40338.60388 R_y,

Table 3 : Énergie totale calculée par FP-LAPW et enthalpie de formation.

Compound	Total Énergie (eV)	Enthalpie of formation(eV)

$PdH_{0.25}$	-548850.493678	-0.577424
$PdH_{0.50}$	-548866.566597	-0.905008
$PdH_{0.75}$	-548882.156051	-1.111738
PdH	-548901.139548	-2.166974

From Table 3, the results show that the formation energies decrease as the number of hydrogen atoms absorbed by palladium increases from 1 to 4 atoms per cell. Although the hydrides PdH_x (x=0.25, 0.50) do not exist in practice (because there are two mixed phases (α+β) in this case), we have noticed that they are roughly stable than PdH. The most stable hydride that has a symmetrical structure (cfc) is the PdH which has the most negative energy.

3.4 Electronic properties

The electronic properties of PdH_x (x = 0 , 0.25, 0.50, 0.75, 1) were calculated as part of the DFT using the WIEN2k code. Table 4 summarize the values of the electronic affinity, ionization energy and electronegativity related to Pd metal and H atoms. We accept that each hydrogen atom brings one electron to the 4d band of palladium, whose Fermi level is moving steadily towards the lower energies. From a chemical point of view, from Table 4, we see that the hydrogen atom can keep its electron because of their electronegativity almost equal to that of Pd. But because of this notable difference, we note the existence of an attraction between the last two atoms.

Table 4: electronic constants related to Pd metal and H atoms.

Atome	Electronic affinity (eV)	Ionization energy (eV)	Electronegativity (Pauli Scale)	Electronegativity (Allred-RochowScale)
Pd	0.518	7.76	2.2	1.35
H	0.702	13.6	2.2	2.2
Activity function of Pd metal			5.12 (eV)	

To know the type of bounds of the Pd-H system, we calculated the following electronic properties:

3.5 Structure of energy bands

The energy bands give the possible energies of an electron as a function of the wave vector. These bands are thus represented in the reciprocal space, to simplify, only the higher symmetrical directions in the first Brillouin area have been treated. For our components Pd and PdH_x (x =

0.25, 0.50, 0.75, 1), the spectra are characterized by the presence of 4d (d, d_{eg}, d_{t2g}) and hydrogen bands. The results we obtain are illustrated in Figure 6.

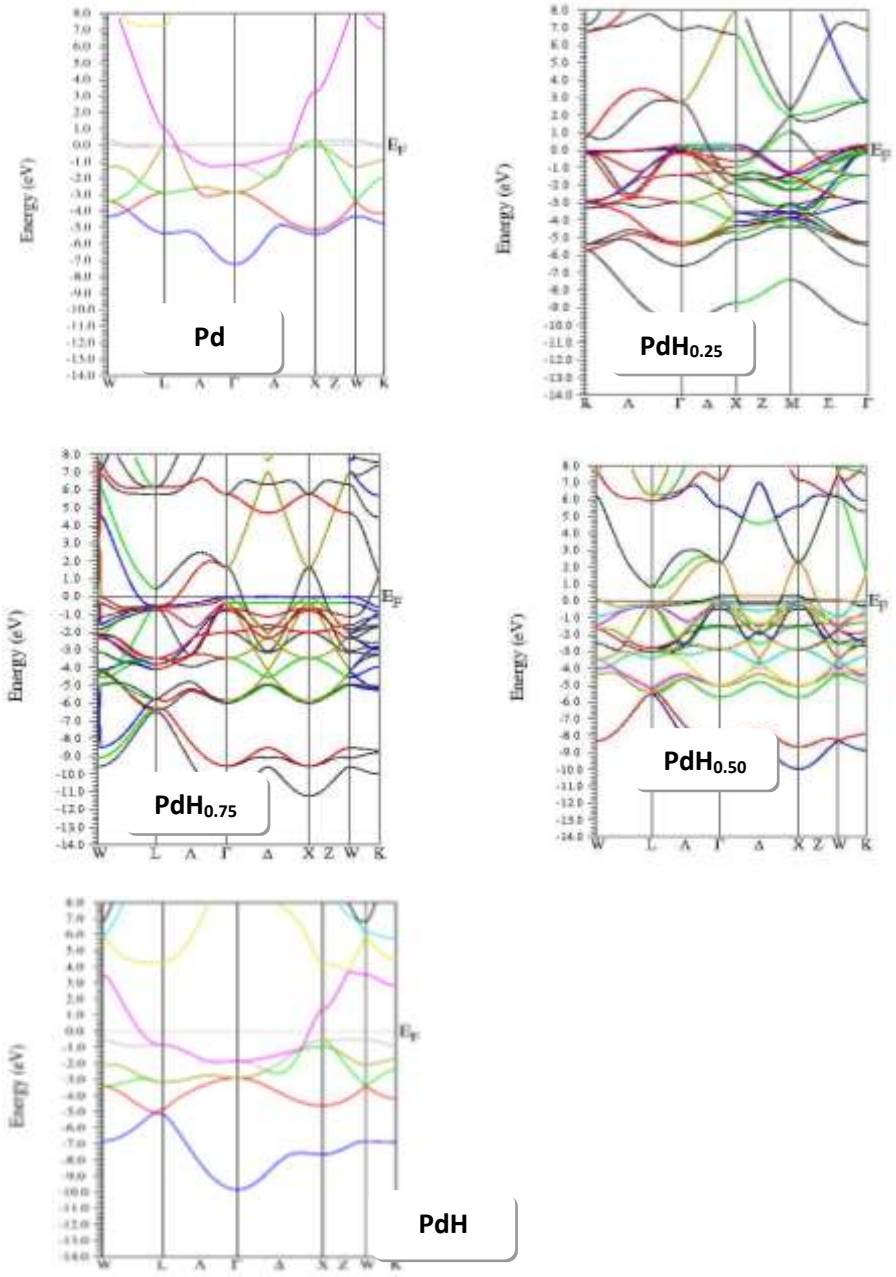


Fig. 6. The energy structure bands of the Pd et de PdH_x (x=0, 0.25, 0.50, 0.75, 1)

The graphs in Figure 6 shows some similarity between the energy band structures, although quantitatively they are different. The materials studied being conductors, the conduction bands are continued. We note that the minima of the conduction bands are at the same point k(0,0,0), precisely at the point Γ of the first Brillouin zone, except with the $PdH_{0.25}$ which also has the same value at point k(1,0,0), precisely at point X. The comparison of the results obtained for

PdH shows that they are very similar to what is reported in references [25][26][27][28]and also for the Pd that is agreed with that of references [29][30].

Density of states (DOS) :

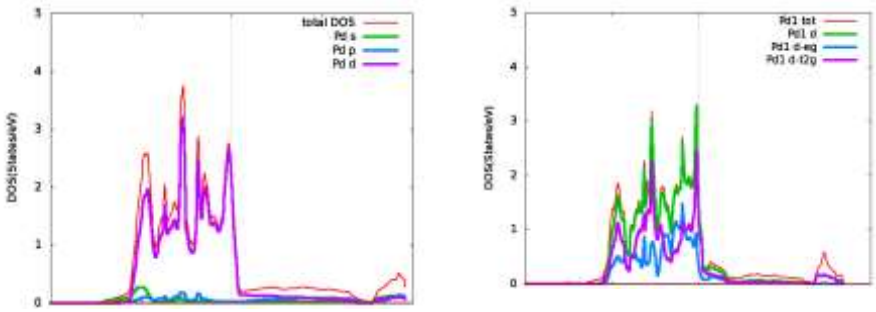
The total state densities (DOS) and partial Pd and PdHx as a function of energy (in eV), the Fermi level taken as zero energy (discontinuous line) obtained by the FP-LAPW method are represented in Figures 7, 8 and 9.

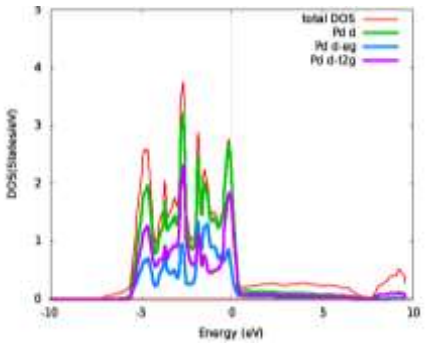
In the materials studied, the valence electrons are of type d (4d of palladium) and s (1s of hydrogen). It is known that the Fermi level is in the pure Pd in the immediate vicinity of a state density peak that gives this metal all particular properties (superconductivity, etc.). The electrons of the hydrogen atoms are located at the two main peaks, one has about 7 eV below Fermi level, where we find a hybridization between their orbits and the orbital d_{eg} of palladium and the other has about 4.2 eV above Fermi level, where we find a hybridization with palladium orbital d_{t2g}.

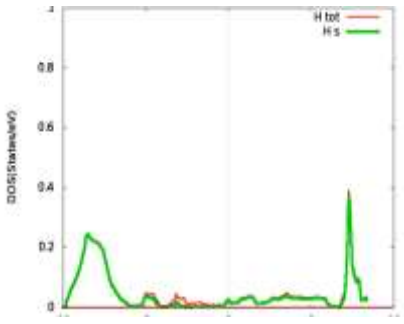
The d_{eg} electrons type of palladium have two intense peaks at -1 eV and -3 eV witch are hybridized with the peaks of the d_{t2g} electrons type, and both another peak at -2 eV d_{eg} and one from d_{t2g} to -2.8 eV.

There is a noticeable shift in densities from PdH_x to low energy with each addition of an H atom, which is consistent with the demonstration of reference [31] for Pd, $PdH_{0.25}$ and PdH, in addition to that of PdH in reference [32].

The effect of hydrostatic pressure on the electronic properties of palladium hydride is related to changes in interatomic distances by the addition of pure palladium.







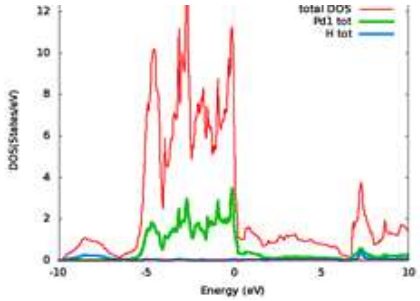
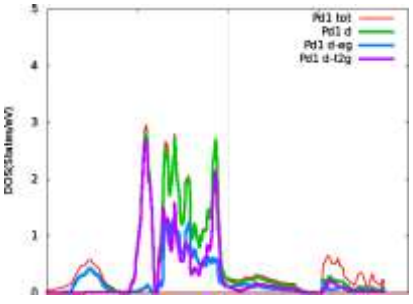
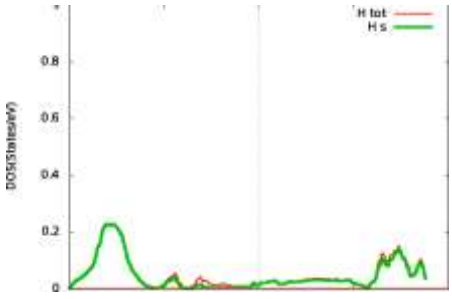
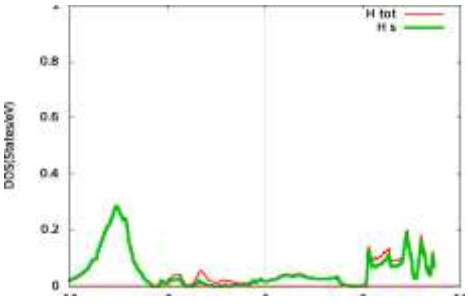


Fig. 7. Partial and total state densities of Pd

Fig. 8. Partial and total state densities of $PdH_{0.25}$







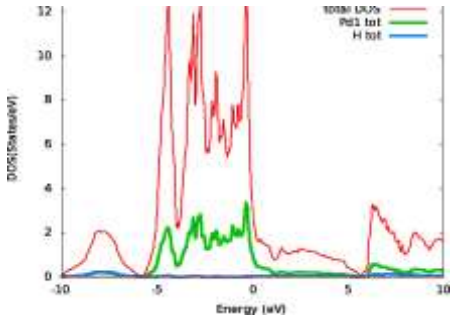


Fig. 9. Partial and total state densities of $PdH_{0.50}$

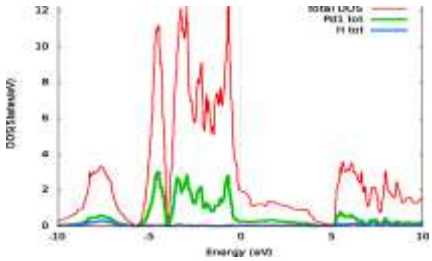


Fig. 10. Partial and total state densities of $PdH_{0.75}$

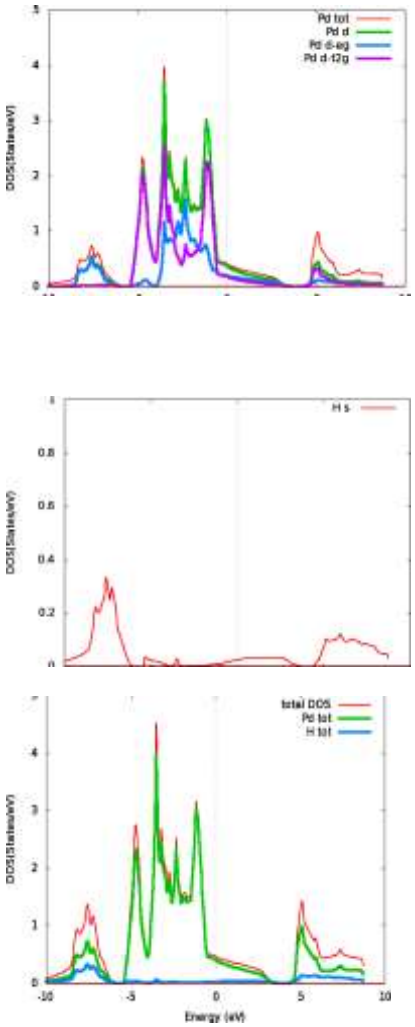


Fig. 11. Partial and total state densities of PdH

Density of electronic charges

It is crucial to understand the density of electronic charges. It allowed us to know the type of bonds established between the palladium and the hydrogen atoms, the binding charge and the origin of the electronic and structural properties. The charge densities are analyzed in the direct space, as opposed to the structure of bands, which is examined in the reciprocal space and can thus provide a realistic representation of the electronic charge distributions. The ionic or covalent character of a solid is related to the distribution of the charge between the constituents. These two characters are related by the following relation:

$F_c + f_1 = 1$

f_c : refers to the covalent factor

f_i : ionicity factor

Pauling [21] defined ionicity in a thermochemical way, while Coulson [34] used the strong bond method (LCAO) for the definition of ionicity. To know the nature and character of the bonds between atoms, and to explain the charge transfer and the bond properties in the case of the materials Pd and PdHx, we calculated the total valence charge densities in the densest plane known as the probability of finding an electron of charge "e" in a certain region of space by the following relation:

$\rho(r) = e \left| \psi(r) \right|^2$

By adding up all of the electronic states k that are occupied by all of the n bands of the crystal, the overall electronic charge density in the crystal can be calculated by the following relation.

$$\rho(r) = 2e \sum_{n,k} \left|\psi_{n,k}(r)\right|^2$$

The calculation of the total ρ(r) charge density requires knowledge of wave functions throughout the Brillouin area. We used the method of representing ρ(r) as a line of equal density, which implies a topographical projection of ρ(r) on a plane passing through the two palladium and hydrogen atoms present in the adjacent cell. The figures (12-17) show the electronic charge density profiles for Pd and PdHx (x = 0.25, 0.50, 0.75, 1) in their cubic cfc structures in which hydrogen is found on octahedral sites. While the figures (18-19) show the profiles of the electronic charge density of the PdH mesh once occupied with the Pd alone, another with the H alone and differential. From Pd's charge density we notice a spherical uniform charge distribution around the palladium confirming a metallic bond.

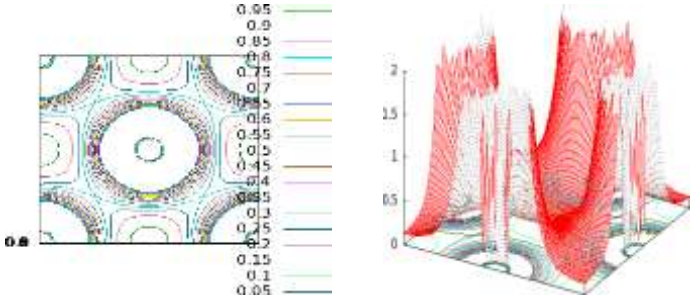


Fig. 12. Pd electronic charge density spectrum in plane 1 0 0

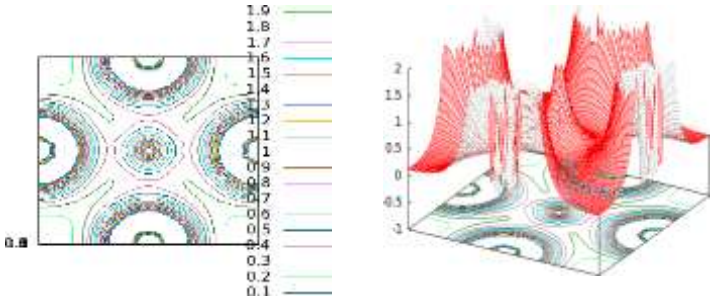


Fig. 13. $PdH_{0.25}$ electronic charge density spectrum ½ 0 0

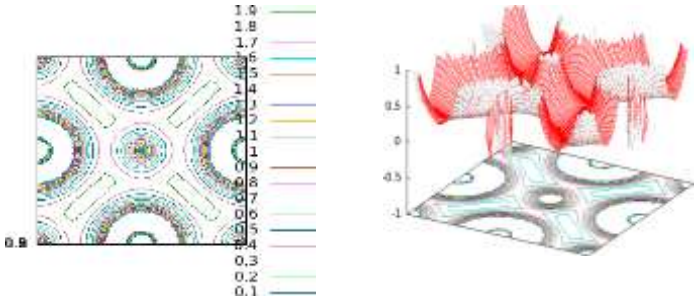


Fig. 14. $PdH_{0.50}$ electron charge density spectrum ½ 0 0

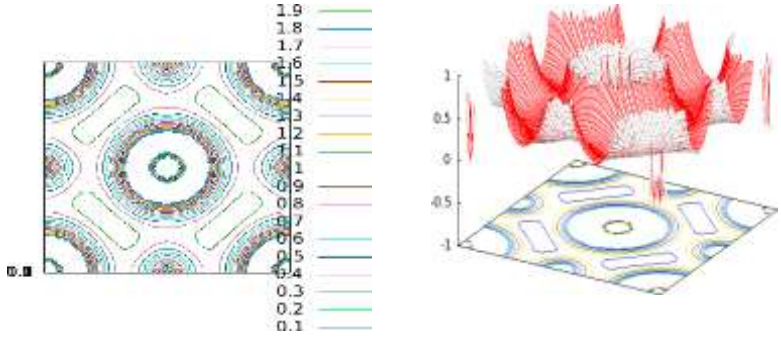


Fig. 15. $PdH_{0.75}$ electronic charge density spectrum at plane 1 0 0

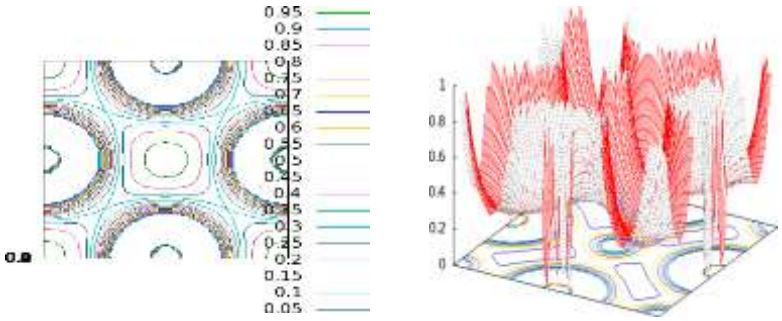


Fig. 16. PdH electronic charge density spectrum ½ 0 0

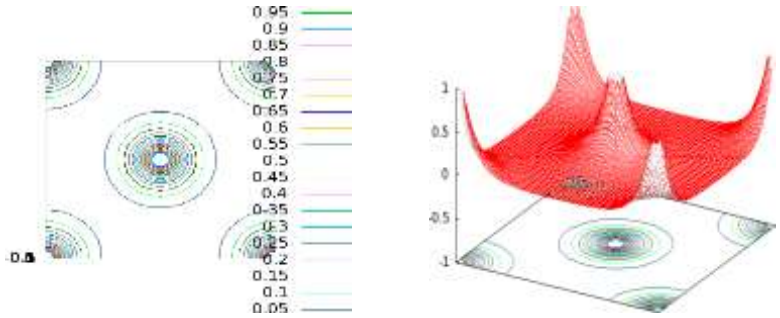


Fig. 17. PdH-Pd charge density in ½ 0 0 plane

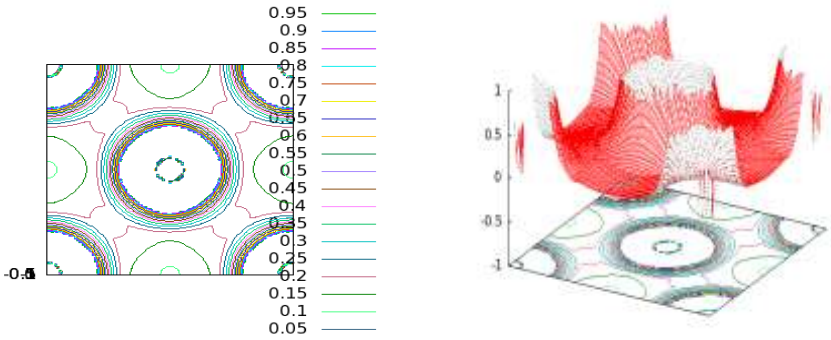


Fig. 18. PdH-H charge density in plane 1 0 0

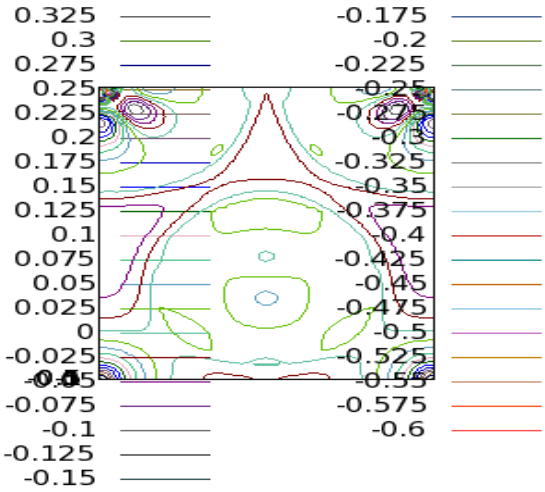


Fig. 19. PdH Differential Charge Density in ½ 0 0 Plane Quarter

We note that these densities of charges have about the same characteristics, each presenting a maximum of charges which is slightly moved towards the vicinity of the palladium. At the hydrogen level, there is a low charge. In addition, another observation can be made that there is a low charge equal to (0.3) at the level of the interstitial regions for all the hydrides studied.

The displacement of the maximum of the charge density towards the palladium side is due to a difference in the potential of Pd and H. these results are qualitatively consistent with those of reference [2] and [35] for Pd and PdH.

However, the density of electronic charges is slightly asymmetrical around the centre of the bond, so the large transfer of charges from cation to anion indicates that anion has a stronger potential than cation. This difference in potential is responsible for the nature of the ionicity present in the bound. So the similarity presented in the sum of the four valence bands indicates that the covalent character is slightly more pronounced than the ionic character for all these compounds.

4. Conclusion

We have successfully calculated the structural properties, the cell parameters and compressibility module of pure palladium and palladium hydride. The results confirm by comparison with the subsequent work a good agreement which allows to say that our results are very acceptable.

Additionally, we have demonstrated that the crystalline network significantly dilates in response to hydrogen absorption. We reached the following findings after looking at the electronic band structures and state densities of pure palladium and its non-sterechiometric hydride: Pd and PdHx substances have metal-like characteristics. As electrons lose energy, there is more of a

binding force between the elements Pd and H, making the system more stable [11]. The hydrogen atom is more electronegative than the palladium atom in the palladium hydride phase [13].

A good amount of hydrogen can be absorbed or released by palladium through to its outstanding structural and electronic properties, but nevertheless, this adsorption and desorption are challenging at temperatures close to room temperature. Therefore, and for a more advanced research on its characteristics, it may be considered to study the thermal equilibrium properties of this system as a function of substitution alloys with other transition metals.

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