Electronic structure of a hydrogen impurity near a (001) Pd surface

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We discuss the adsorption and absorption of light impurities (H) near a transition-metal surface (Pd), within the framework of the electronic structure of interstitial impurities. We derive the band structure and total energy of the system H/Pd(001) in a tight-binding model, taking into account s, p, d orbitals of Pd. We obtain the relative stability of the various sites (tetrahedral and octahedral sites), relative to their position to the surface, from adsorption to absorption. The "bridge" geometry is found to be the stablest adsorption site with an energy in agreement with experiment. Some "subsurface" sites are also very stable ones. The coupling strength between the 1s orbital of hydrogen to the 5s orbital of Pd is an essential parameter. We argue that the interactions between H atoms, even at small finite concentration, can qualitatively alter the results obtained in the infinitely dilute impurity result.

I. INTRODUCTION

The electronic structure of hydrogen adsorbed or absorbed in transition metals is a much studied subject, both theoretically and experimentally. The high ability of hydrogen absorption in transition metals like Pd and Nb made the latter good candidates for energy storage.[1] Hydrogen yields also to embrittlement and degrades the mechanical properties of these metals.[2] Many recent conferences are devoted to these subjects.[3,4] Christmann[5] reviewed the surface properties of hydrogen adsorbed on transition metals. Another point of interest for this system are the hydrogenation catalytic properties of Pd.[6]

Recently, some of us[7] (hereafter referred to as I) developed the formalism for studying the electronic structure of an isolated impurity near a metallic surface. In the present paper we apply it to a hydrogen impurity near a Pd(001) surface. We consider various environments (octahedral and tetrahedral sites) relative to the surface, from adsorption (surface) up to absorption (bulk).

The evidence for "subsurface" chemisorption has been proven by angleresolved photoemission spectroscopy on the Pd(111) surface by Eberhardt et al.;[8] these results were confirmed by Felter et al.[9] Theoretical models supporting this fact have been developed by ourselves (I) and Chan and Louie.[10] In the case of the Pd(110) surface also, low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS),[11] as well as He scattering[12] confirmed subsurface chemisorption.

One of our purpose is to study the stability of such "subsurface" adsorption sites of hydrogen on a Pd(001) surface, in the dilute limit. It is the simplest model available in order to study this trend. Contrary to more elaborated models, no periodicity is required and any position of the impurity can be studied.

In Sec. II we briefly recall the formalism; in Sec. III we apply it to the Pd(001)-H system.

II. FORMALISM

In the tight-binding scheme, we describe an interstitial impurity within the following model: a semi-infinite host

I, of Hamiltonian H_I^0 coupled through the Hamiltonian terms $H_{IA} + H_{AI}$ to a free adatom A of Hamiltonian H_A^0. The total basis is the reunion of both subspaces I and A. The total Hamiltonian is

$$H = H_I^0 + H_A^0 + \Delta H_I + \Delta H_A + H_{IA} + H_{AI} . \quad (1)$$

ΔH_I (ΔH_A) acts only on subspace A (I). This approach has already been developed by Grimley and Pisani[13] in the case of the adsorption.

The dissolution energy which we define here as the energy difference between the coupled and uncoupled system ($H_{AI} = H_{IA} = \Delta H_I = \Delta H_A = 0$) accounts for the relative stability of any position of the adatom within the semi-infinite host. It can be written as

$$E_{\text{tot}}(R) = E_{\text{BS}}(R) + E_{\text{BM}}(R) , \quad (2)$$

where R denotes the position of the impurity,
$E_{\text{BS}}(R)$ the electron band-structure contribution

$$E_{\text{BS}}(R) = E_{\text{BS}}^1(R) - E_{ee} . \quad (3)$$

$E_{\text{BS}}^1(R)$ is the one-electron band-structure contribution; E_{ee} accounts for the electron-electron interactions, which are counted twice in the one-electron energy. E_{ee} can be written as within some approximations:[14]

$$E_{ee} = \frac{1}{2} \sum_{i,\alpha} \delta E_i^\alpha \int_{-\infty}^{E_F} n_i^\alpha(E) dE , \quad (4)$$

$n_i^\alpha(E)$ is the local density of states (LDOS), δE_i^α the variation of the matrix element of the potential on the site i of symmetry α, E_F the Fermi level. We mention that in the case of hydrogen, the atomic reference state causes some trouble; therefore we considered the relative variation of this term with respect to the bulk position.

$E_{\text{BM}}(R)$ accounts for the ion-ion repulsion. We describe it by a sum of pair interactions, in the phenomenological Born-Mayer approach,

$$E_{\text{BM}}(R) = \sum_{R_{ij}} A \exp(-p R_{ij}) , \quad (5)$$

considering the pairs R_{ij} formed by the impurity i located

at R and its host nearest neighbors j. One could also take into account the atomic relaxations of the host with relation (5), and adequate parameters A and p.

Assuming that the impurity potential is localized, we ensure the global charge neutrality (Friedel sum rule[15]), and we express the one-electron band-structure term and the local density of states on the impurity as a function of its position relative to the surface (I). Only the knowledge of the Green's functions of the unperturbed host is required in our model. Our formalism applies easily to a host with low symmetry, in the presence of a surface, for instance. Within the generalized phase-shift formalism, we obtain a closed expression for the dissolution energy, in case of a localized potential, without further hypothesis. This simplicity is lost if we extend the perturbation beyond the impurity site, on the first neighboring sites for instance; the populations are also modified in that case.

III. AN ISOLATED HYDROGEN IMPURITY NEAR A Pd(001) SURFACE

We apply this formalism to an isolated hydrogen impurity dissolved or adsorbed near or into a Pd(001) surface. The calculation is performed in two steps: First we determine the self-consistent electronic structure of a semi-infinite Pd crystal with a (001) surface and then we place the hydrogen adatom into the octahedral or tetrahedral sites, and we discuss the dissolution energy and stability of these locations relative to the surface. We take into account the s, p, and d orbitals of the Pd substrate. We use Papaconstantopoulos et al.[16] hopping integrals up to second Pd neighbors. We adopted the following hypotheses in order to build the semi-infinite medium: We force every atom to remain neutral and we allow intraatomic charge transfers between s,p orbitals only;[17] thus we have to determine two parameters for each atomic plane. The effects of the presence of the surface are sensitive on the first three planes from the surface only.[18] After this step, we consider the hydrogen impurity coupled to semi-infinite host. We neglect any relaxation effects around the impurity site and we limit the range of the perturbating potential to the impurity site. As in paper I, this unique parameter is determined by the use of the Friedel's sum rule.[15] The band-structure energy is then given in terms of chemisorption matrix elements, which depend only on the Green's function elements of the pure substrate. They are computed with the use of the recursion method,[19] as continued fractions, up to 14 exact levels. The prescription of Beer and Pettifor[20] has been used to determine asymptotical values of the coefficients of the continued fractions. The hopping integrals s_i between 1s hydrogen orbital and the s, p, and d Pd orbitals are given by Faulkner.[21] The work function of Pd is 5.12 eV.[22] The atomic level of the isolated hydrogen atom is -13.26 eV.[23] The hopping integral dependence versus the distance of the H 1s orbital with a neighboring metal orbital at distance R is parametrized as in Ref. 24,

$$s_i(R) = s_i^0 \exp[-3(R/R^0-1)], \quad i=s,p,d . \quad (6)$$

R^0 denotes the corresponding bulk octahedral distance. In our present work we avoided the explicit determination of A and P parameters by deriving the global parameter $\alpha = A \exp(pR_{ij})$ from experimental dissolution energy (octahedral) or diffusion barrier heights (tetrahedral). Since we did not allow geometrical relaxation, we just had to examine the coordination of various sites. In Table I we indicate the environment and coordinates of impurity sites we study. In Table II we report the variation of the total dissolution energy E_{tot}, as defined in Eq. (2).

A. Preferential adsorption position

The bridge position (tetrahedral, twice coordinated) is found to be the stablest adsorption position with an adsorption energy of -2.93 eV. This value is close to the experimental value of Behm et al.[25] (-2.77 eV). With a value of the adsorption energy of -2.49 eV, the hollow position is less favorable than the bridge one, but is more favorable than the on-top position (-2.03 eV). Various experimental results of ordered phases of hydrogen on Pd(001) led to the evidence of adsorption in a hollow site. $c(2\times2)$ ordered phases on Pd(001) were studied by He scattering (Rieder and Stocker[26]) as well as by electron-energy-loss spectroscopy (Nybeerg and Tengstal[27]). Only Behm et al.[25] studied this system at lower coverages of hydrogen by LEED, thermal desorption, and work-function measurements. Recently Tomanek et al.,[28] in an ab initio pseudopotential local-orbital method, found that the hollow site is the stablest, with an adsorption energy of -2.92 eV, followed by the bridge one (-2.50 eV) and the on-top one (-1.86 eV). Muscat,[29] with the embedded cluster method, found that the bridge position or a threefold coordinated one just below the surface plane can be the stablest one. However, the interactions between H atoms, even at small finite concentration, can qualitatively alter the results obtained in the infinite dilute limit. For the on-top position, the impurity has only one Pd atom as a neighbor; the localized potential hypothesis fails since it induces a large charge transfer which would also require to extend the range of the perturbation to achieve selfconsistency. In that peculiar case we assume therefore the local charge neutrality, which provides a better model for the physical system described within a localized scheme.

B. Subsurface positions

For these positions, since we neglect any geometric relaxations, the Born-Mayer repulsion term is the same as in the bulk. We find that the tetrahedral position just

TABLE I. The studied geometries of an interstitial atom in fcc Pd: The label n indexes the position of the interstitial atom (in units $a/2$ of the lattice parameter) for the (001) surface. Usually $n=-1$ refers to an adsorption position; $(x,y,0)$ with x and y integers denotes a host site in the surface plane.

Octahedral site for n even	$(1,0,n)$
Octahedral site for n odd	$(1,1,n)$
Tetrahedral site	$(1/2,1/2,1/2+n)$

TABLE II. The one-electron band-structure energy (E_{BS}), the Born-Mayer term (E_{BM}), the electron-electron interaction (E_{ee}), and the total dissolution energy (E_{tot}) of an H impurity in (001) Pd vs its position (n is given in Table I). All energies are in eV. For the octahedral positions $(ss\sigma)=1.19$ eV, $(sp\sigma)=2.20$ eV, and $(sd\sigma)=1.63$ eV (Ref. 21); for the tetrahedral positions $(ss\sigma)=1.78$ eV, $(sp\sigma)=3.30$ eV, and $(sd\sigma)=2.44$ eV.

n	E_{BS}	E_{BM}	E_{ee}	E_{tot}	
			Octahedral positions		
-1	-3.127	0.640	-0.460	-2.027	on-top
0	-7.083	5.107	0.509	-2.485	hollow
1	-8.411	6.128	0.004	-2.283	subsurface
2	-8.895	6.128	-0.089	-2.678	subsurface
3	-8.520	6.128	0.072	-2.463	subsurface
bulk	-8.488	6.128	0.000	-2.360	bulk
			Tetrahedral positions		
-1	-6.173	3.420	0.179	-2.932	bridge
0	-7.775	6.841	0.464	-1.400	subsurface
1	-9.920	6.841	-0.466	-2.613	subsurface
2	-9.171	6.841	-0.055	-2.275	subsurface
3	-9.079	6.841	-0.048	-2.190	subsurface
bulk	-8.971	6.841	0.000	-2.130	bulk

below the surface plane is highly unfavorable with an adsorption energy of -1.40 eV. But the next tetrahedral position ($n=1$) with an energy of -2.61 eV and also the following octahedral position ($n=2$) with an energy of -2.68 eV are favorable. This indicates that, in the dilute impurity phase (neglecting interactions between impurities), subsurface preferential adsorption occurs into these positions. Farther from the surface, the total dissolution energies E_{tot} converge toward the bulk values: -2.36 eV for the octahedral position, which is the equilibrium position in the bulk,[30] and -2.13 eV, the value given by Alefeld and Völkl[31] for the tetrahedral bulk position. As pointed out earlier in I, the concentration profile in the dilute impurities limit is nonmonotonous.

C. Local densities of states

In Fig. 1 we report the local densities of states for various positions of the hydrogen impurity. For the octahedral sites, which are the bulk equilibrium positions for the α PdH hydride, we find near the bottom of the band an intense peak, almost completely split from the band. Since the asymptotical values of the coefficients of the continued fractions have been computed in a coherent way, the termination of Pettifor and Beer provides the correct spectral width.[20] This result agrees with the photoemission data of Eastmann et al.[32] Previous calculations of the electronic structure of an isolated hydrogen impurity in Pd indicated the possibility of the presence of a bound state below the 1s H band; it is found very close of the bottom of the band by Klein and Picket[33] and by Khalifeh and Demangeat,[34] much lower (about 4.3 eV) by Yussouff and Zeller.[35] As in Refs. 33 and 35 this low-lying band is also found in calculations for stoichiometric PdH.[16,36] The electronic occupation for the octahedral bulk position on the hydrogen site is 0.65 electron (Table III). According to some other calculations[16,21,36,37] we

find a charge transfer from the hydrogen to the Pd neighbor sites. This point remains unclear, since some other authors[34,35,38] have found the opposite sign for this charge transfer; the same trend is observed in cluster calculations.[39] In the tetrahedral bulk position, we find also a low-lying band with a split peak. The electronic occupation is low (0.59 electron).

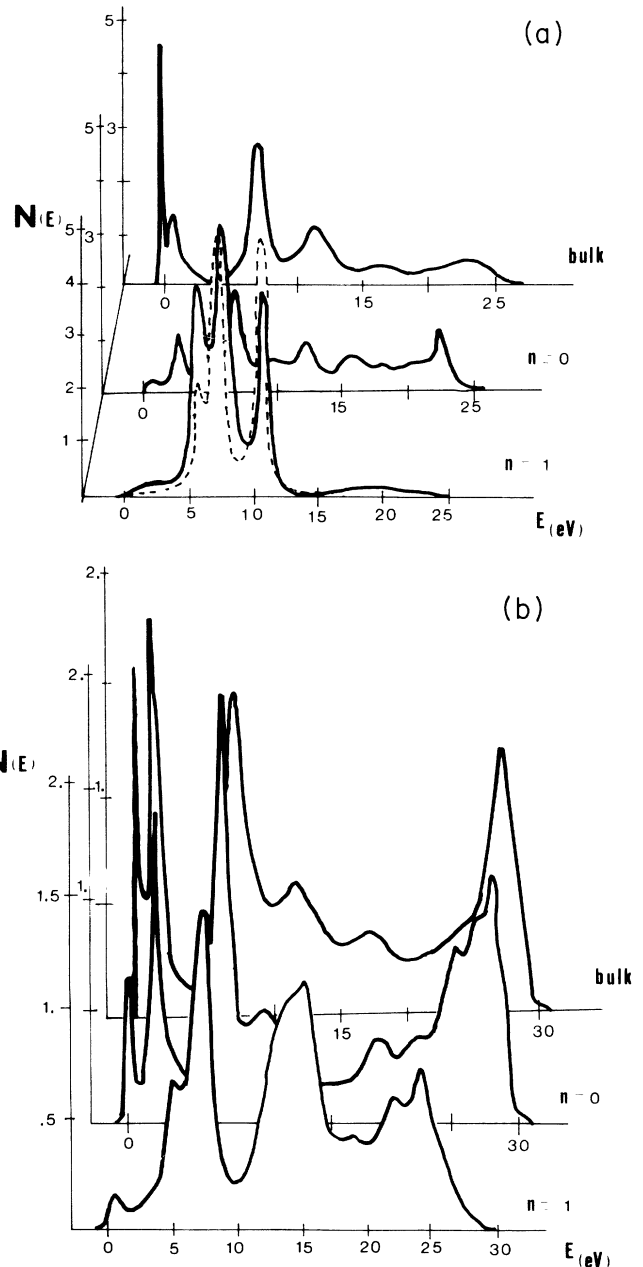This low-lying band, observed for the octahedral position, disappears when the impurity is located in the octa-

FIG. 1. Local density of states on the hydrogen interstitial site in Pd(001) vs energy and the position of the impurity given by the label n, defined in Table I. The hopping integrals between H 1s orbital and the Pd s, p, and d orbitals are given by Faulkner (Ref. 21). (a) Octahedral positions (note for $n=-1$ in the solid line, the local neutrality is ensured, in the dashed line, only the global neutrality is ensured). (b) Tetrahedral positions.
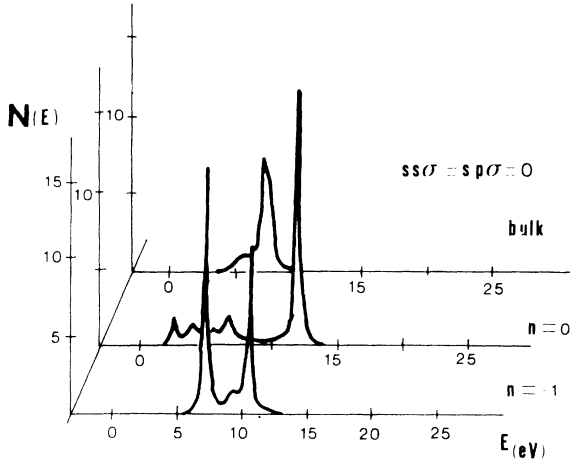
FIG. 2. Local density of states on the hydrogen octahedral site in Pd(001) vs energy and position of the impurity given by the label n defined in Table I; the values of the hopping integrals H-Pd are $(ss\sigma)=(sp\sigma)=0$, $(sd\sigma)=1.63$ eV.

preceding calculation $((ss\sigma)$, $(sp\sigma)$, $(sd\sigma)$ nonvanishing) disappears as soon as one considers only $sd\sigma$ coupling (Fig. 2 and Ref. 40) or $sp\sigma$ coupling only.[18] A strong ionicity on H is observed (Table III) in the bulk position with $sd\sigma$ coupling only (as in paper I). Our results rely also upon the phenomenological scaling law used for the hopping integrals [Eq. (6)]. For the tetrahedral sites, an alternative choice with integrals scaled as[18]

$$(si\sigma)=(si\sigma)^0 \exp[-4(R/R^0-1)] \tag{7}$$

has been tested. We find that the results (total energies, electronic occupations) are quite insensitive to this choice. For sake of completeness, in order to compare with other authors, we inferred the values of pR^0, assuming Eq. (7) for the hopping integral scaling: we obtain $pR^0=4.5$. This value is somewhat smaller as usually assumed.[41] But we recall that we lumped the ionic repulsion term with the electron-electron contribution in the bulk.

The presence of the surface affects the local density of states on the impurity site and thus the global one-electron band-structure energy. We find a band narrowing caused by the surface: It is the most important for the on-top adsorption position, where the hydrogen atom interacts only with one Pd atom. This trend is also observed for the hollow position, where the coordination of the impurity is 5 [Fig. 1(a)].

Our model could be improved by extending of the perturbating potential on the direct neighboring of the impurity. The single-site approximation, made in this work, is, a priori, quite crude. A fully self-consistent scheme would require to extend, at least on the first shell of neighbors of the impurity, the perturbating potential. This potential can be written as[42]

$$V_p(R)=\sum_i U_{ii}\,\delta N_R^i + \sum_{j\neq i, R\neq Q} V_{RQ}^{ij}\,\delta N_Q^j, \tag{8}$$

where i and j label orbitals, U^{ii} is the intra-atomic Coulombian integral, V_{RQ}^{ij} is the interatomic Coulombian integral between the sites R and Q, and δN_R^i is the variation of charge on the site R for the orbital i (the initial state would be here the local neutrality).

This problem has been solved by considering the V_p term as a perturbation in the case of hydrogen in an infinite host of Pd.[43] Surprisingly, in all these cases, V_p has been found to be very small (of order of hundredths of eV). This point can be understood as following. Let H be the impurity site and R a first neighbor site. In Eq. (8) we have to take into account the second term involving interatomic integrals. Contrary to the case where only d orbitals are interacting,[42] this term cannot be neglected. The main contribution arises from the hydrogen site. The ratio of $\frac{1}{8}$ is usually assumed for V_{RR}^{ij}/U_{RR}^{ii}.[42] Roughly, we estimate for Z first neighbors $\delta N_H = -Z\,\delta N_R$ and $U^{ss}=kU^{dd}$ with $k=2-3$. Supposing that the term V_{RH}^{is} is the geometric or arithmetic mean of U_{HH}^{ss} and U_{RR}^{ii}, the term $V_{RH}^{is}\,\delta N_H$ can counterbalance the first term of Eq. (8). For these reasons, the final value of V_p is small and moreover one cannot pre-

hedral adsorption site, as long as the global neutrality only is ensured. The same trend is observed in the tetrahedral case. We have no major difference for the on-top adsorption site with either the local or global neutrality, as can be inferred from Fig. 1(a). The three peaks remain at the same position, with very small intensity differences.

IV. DISCUSSION

In this section we discuss the validity and accuracy of the model, and the various approximations made in this work. We have introduced the coupling between the $1s$ orbital of H and s, p, d orbitals of the transition-metal substrate (only d orbitals were considered in paper I). The H $1s$–Pd sp coupling (Fig. 2 and Ref. 40) is essential in Pd: the low-lying structure in the local density of states of hydrogen, which exists for the values used in the

TABLE III. Electronic occupation on an H impurity in (001) Pd vs its position (n is given in Table I). Note that for the adsorption octahedral position we have imposed the local neutrality (within parentheses, global charge neutrality only). The value of the Fermi level is 7.13 eV.

		Occupation	
n	Octahedral	Tetrahedral	Octahedral
-1	1.0 (0.715)	0.397	0.496
0	0.495	0.522	0.563
1	0.690	0.718	1.308
2	0.675	0.616	1.472
3	0.623	0.614	1.471
bulk	0.654	0.597	1.482
	Resonance parameters		
$ss\sigma$	1.19	1.78	0.0
$sp\sigma$	2.20	3.30	0.0
$sd\sigma$	1.63 [a]	2.44	1.63

[a] Reference 21.

dict its sign. If we consider now the case of a semi-infinite host, the problem is more delicate, since the system has a reduced symmetry; thus the Pd neighbors of the impurity are inequivalent. The number of parameters will grow too much, and credible estimates become awkward.

Let us note the importance of the E_{ee} term of the total dissolution energy. This term, representing the electron-electron interaction counted twice in the one-electron band-structure term, can be of order 0.5 eV (Table II). This term counterbalances the one-electron band-structure energy (E_{BS}). It is therefore essential to take it into account, especially for the tetrahedral case. In fact, here we have supposed no contribution of E_{ee} for the bulk positions, since it is well known that the isolated atomic hydrogen cannot be considered as a good reference state; the variation of the potential E_{ee} is due the electron-electron Coulomb interactions only.

Finally let us mention that formally, another approach for this problem is possible. The total energy can be written as the sum of "atomic" energies expressed in terms of the local densities of states. The recursion method can be used to compute these latter quantities. This approach is fruitful in the case of small atomic relaxations, provided the parametrization of the hopping integrals and the Born-Mayer repulsion is valid and accurate. It is possible to determine the barrier heights in this framework.

In summary we have determined the electronic structure of an hydrogen isolated impurity near a Pd(001) surface within the tight-binding theory, for any position of the impurity. We find the bridge adsorption position to be stablest one with an adsorption energy of -2.93 eV. The discrepancy with the experimental data at finite coverage (the hollow position is the stablest adsorption position) is not incompatible with our result, valid in the very dilute limit only. Only Behm et al.[21] considered small coverages of hydrogen. Even at such hydrogen concentration (0.25), the impurity-impurity interactions, neglected in this work, may modify significantly our results. A further study including these interactions is in progress.

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