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<sup>8</sup>T. H. Upton and W. A. Goddard, III, *J. Am. Chem. Soc.* **100**, 5659 (1978).

<sup>9</sup>As the  $3d$  orbitals of Ni are quite tightly bound, Coulomb and exchange integrals involving these orbitals are large ( $J_{dd} \approx 1.0$  hartree = 27 eV). Thus, it is of utmost importance that the correct open-shell Hamiltonian be used in solving for these orbitals. Anomalous large amounts of  $4s$ - $3d$  mixing result when the  $3d$  orbitals are forced to become delocalized through use of the incorrect or approximate Hamiltonians.

<sup>10</sup>T. H. Upton and W. A. Goddard, III, *J. Am. Chem. Soc.* **100**, 321 (1978); S. P. Walch and W. A. Goddard, III, *Solid State Commun.* **23**, 907 (1977); G. A. Ozin, W. J. Power, T. H. Upton, and W. A. Goddard, III, *J. Am. Chem. Soc.* **100**, 4750 (1978).

<sup>11</sup>An effective potential was used to replace the Ar

core initially [M. J. Sollenberger, M. S. thesis, California Institute of Technology, 1975 (unpublished)], and then further modified to replace the  $3d^9$  core as well using the method of C. F. Melius, B. D. Olafson, and W. A. Goddard, III, *Chem. Phys. Lett.* **28**, 457 (1974).

<sup>12</sup>Basis sets were those ( $4s$ ) of S. P. Walch and W. A. Goddard, III, *J. Am. Chem. Soc.* **100**, 1338 (1978). H-atom basis sets were  $DZ$  (unscaled) from S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

<sup>13</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1950).

<sup>14</sup>Similar conclusions have been drawn from extended Hückel studies (Ref. 4); however, the predicted trend in binding energies is linear > bridge > fourfold, which is the reverse of that obtained here.

<sup>15</sup>F. J. Himpsel and D. E. Eastman, *Phys. Rev. Lett.* **41**, 507 (1978).

## Hydrogen on Pd(111): Self-Consistent Electronic Structure, Chemical Bonding, and Photoemission Spectra

Steven G. Louie

*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

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The electronic properties of H chemisorbed on the Pd(111) surface are studied using a self-consistent pseudopotential mixed-basis method. The H atoms are predicted to prefer a threefold hollow over the top site. Strong bonding between hydrogen and the substrate results in (a) dramatic changes in the surface electronic structure and (b) the formation of bonding and antibonding adsorbate states. The combined effects of both accurately reproduce and explain the salient features of recent photoemission measurements.

The interaction of hydrogen with group-VIII transition-metal surfaces (Ni, Pd, Pt, ...) is fundamental to the understanding of a number of physically interesting and technologically important processes. These include the dissociative chemisorption and reactivity of hydrogen on the surfaces of these metals and the solubility of atomic hydrogen (hydrogen-storage technology) in these metals. Our knowledge of H chemisorption on transition-metal surfaces is, however, quite limited. Previous theoretical (jellium-H, parametric tight-binding, and cluster) studies<sup>1</sup> have provided a partial picture but none of them is capable of properly describing all the known aspects of the problem. For example, a full understanding of the H-induced structures found in recent photoemission measurements and the answer to the simple, yet crucial, question of the adsorption site have been lacking.

In this Letter the results of a realistic, fully self-consistent calculation describing H chemisorption on a transition-metal surface are pre-

sented. The system observed experimentally is an ordered ( $1 \times 1$ ) monolayer of atomic hydrogen on the Pd(111) surface.<sup>2</sup> Since the adsorption site is unknown, calculations were performed for the three different high-symmetry structural geometries. Unlike previous theoretical approaches,<sup>1</sup> the full effects of the underlying band structure and of the various interactions (Pd-Pd, H-Pd, and H-H) at the surface are treated on an equal footing and in a self-consistent, parameter-free fashion.<sup>3</sup> Comparison of the calculated results with experimental spectra<sup>4,5</sup> shows that the H atoms prefer a threefold hollow over the top site. Strong bonding between the H  $1s$  orbital and the Pd  $d$  electrons is observed which results in dramatic changes in the Pd surface electronic structure. In the preferred geometry, both an occupied H-Pd bonding surface band centered at 6.5 eV below  $E_F$  (in excellent agreement with experiment) and an unoccupied antibonding H-Pd surface band are found. Moreover, with only initial-state effects included, the theory repro-

duces the salient features observed in recent photoemission measurements.

The calculations employ (a) self-consistent pseudopotential theory using the local-density description of exchange and correlation effects, (b) the mixed-basis (plane waves plus  $d$ -like Gaussians) technique,<sup>6,7</sup> and (c) the supercell description of the surface geometry. The only input to the calculations is (1) the atomic positions and (2) the bare ionic pseudopotentials (constructed from free-atom calculations) for the  $\text{Pd}^{+10}$  and the  $\text{H}^{+1}$  ion cores. Both the  $\text{H}^{+1}$  pseudopotential<sup>8</sup> and the  $\text{Pd}^{+10}$  pseudopotential<sup>6,7</sup> have yielded accurate self-consistent results in previous studies of other systems. For the present unit cell, which contains seven layers of Pd with one layer of H on each surface and a vacuum region equivalent to four atomic layers of Pd, convergent energies and screening potentials are obtained with  $\sim 300$  plane waves plus 35 local orbitals (five for each Pd atom) in the basis set.<sup>9</sup>

The three structural models I have considered for the adsorption sites are the following: (A) a monolayer of H directly on top of every surface Pd atom; (B) a monolayer of H in the  $b$  stacking position of the  $abcabc\dots$  stacking sequence of the fcc (111) direction if the terminating Pd layer is in the  $a$  position; and (C) a monolayer of H in the  $c$  stacking position. These three sites constitute the most likely (high-symmetry) positions in which the structureless H atom will adsorb since the surface is a hexagonal-closed-packed plane. Geometrically, the only difference between structures B and C is the position of the second-layer Pd atoms. For all three geometries the H-Pd interplanar distance is determined by taking the H-Pd bond length to be the sum of the Pd metallic radius (1.37 Å) and the H covalent radius (0.32 Å).

The calculated results show that sites B and C produce very similar spectra which agree with photoemission measurements and decisively rule out site A as the preferred site. We therefore first discuss the case of site C. The hydrogen adatoms induce extensive changes in the surface energy-band structure of clean Pd(111) (Fig. 1). The prominent hydrogen-induced features are the appearance of the H-Pd bonding adsorbate band below the Pd  $d$  bands and of a rather dispersive ( $\sim 4$  eV) band of antibonding H-Pd states in a gap just above  $E_F$  near  $\bar{K}$  in the projected band structure (PBS). The effects of hydrogen chemisorption on the intrinsic surface states (resonances) of clean Pd(111) are different de-

pending on the individual states: Some disappear, some move to lower energies, and some change their character. The solid curves in Fig. 1 (between  $-4$  and  $0$  eV) depict the position of the modified Pd surface states.

The wave functions of the H-Pd adsorbate states are found to be almost completely localized on the H and the first Pd layer (which explains the virtually identical surface band structure for sites B and C) and are mostly  $d$ -like surrounding the surface Pd atoms. The strong chemisorption bonding at the surface therefore arises predominantly from the interactions between the hydrogen  $1s$  and the Pd  $d$  orbitals. As an illustration, the charge distributions for the adsorbate states at  $\bar{K}$  are presented in Fig. 2. Small-cluster calculations<sup>10</sup> have previously deduced the existence of the occupied adsorbate band. But, because of the neglect of substrate periodicity, its exact energy, dispersion, and wave function character could not be obtained. Moreover, the existence and the nature of the unoccupied adsorbate states are tied crucially to the PBS of Pd. Therefore, they are difficult, if not impossible, to deduce from small-cluster calculations.

Figure 3 depicts the theoretical surface density of states (SDOS) together with the bulk DOS. The most noticeable effects of H chemisorption are the presence of the state-density peak at  $-6.5$  eV and the drastic reduction of state density near  $E_F$ . The latter effect is due principally to the removal of intrinsic surface states (resonances)

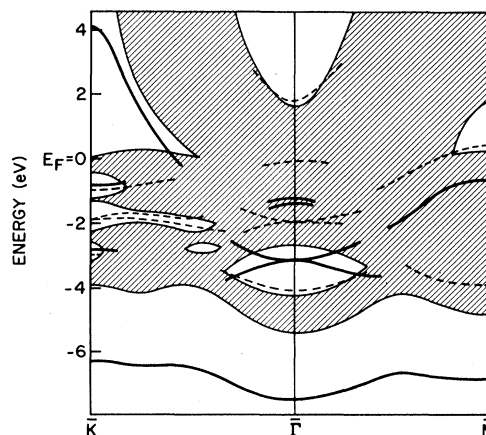


FIG. 1. Localized states (solid curves) and the PBS (shaded areas) in the  $\bar{K} = (2\pi/a)(0, -\frac{2}{3}, \frac{2}{3})$  and  $\bar{M} = (2\pi/a) \times (-\frac{1}{3}, -\frac{1}{3}, \frac{2}{3})$  directions for the H-chemisorbed Pd(111) surface with H in the C site. Also indicated are the surface states (dashed curves) for the clean surface.

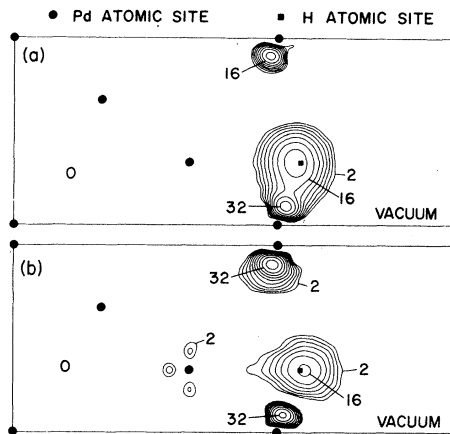


FIG. 2. Charge density contour plots for adsorbate states at  $\bar{K}$  at (a)  $-6.3$  eV and (b)  $4.1$  eV. The charge densities are normalized to 1 electron per unit cell and plotted for a (110) plane cutting the (111) surface.

from this energy region (Fig. 1). It is interesting to compare the present results to that of the PdH alloy system. Both theoretical and experimental data<sup>11</sup> show a similar H-induced structure in the DOS of PdH. However, the peak is much broader in the bulk compound and is located at  $-5.4$  eV. The latter indicates a weaker bonding which is consistent with the finding that the heat of formation for PdH is only half the adsorption energy of hydrogen on Pd(111).<sup>2</sup> Another feature of the

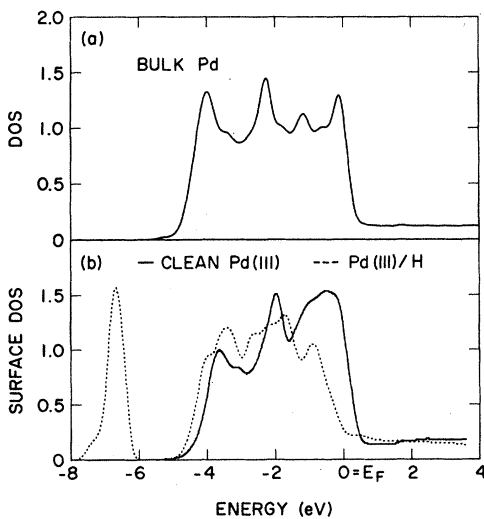


FIG. 3. Calculated local DOS for (a) bulk Pd and (b) Pd(111) surface with and without a monolayer of H in the C site.

self-consistent SDOS is that, unlike predictions from simple Anderson-Newns-like calculations,<sup>12</sup> there is no peak in the spectrum which corresponds to the antibonding H-Pd states. This again is a band-structure effect. An examination of the surface band structure (Fig. 1) shows that the antibonding H-Pd states exist, but are very dispersive and can only exist as bona fide localized states in a very limited region of the two-dimensional Brillouin zone (2DBZ).

The present results are amenable to a *posteriori* interpretation in terms of the Anderson-Newns model of chemisorption. The interaction between the hydrogen and the  $d$  states of Pd is stronger than the  $d$  bandwidth, leading to the formation of well-defined surface-molecular bonding and antibonding states. The interaction between these "molecular" states and the  $s-p$  continuum, while strong, is small compared to the effectively infinite width of the  $s-p$  band. The bonding and antibonding states are therefore broadened by an amount proportional to the state density of the portion of the  $s-p$  continuum with which they are degenerate; the bonding states which lie below the  $s-p$  continuum remain well defined, while the antibonding states become broad resonances in most part of the 2DBZ.

In comparing the calculated results to experi-

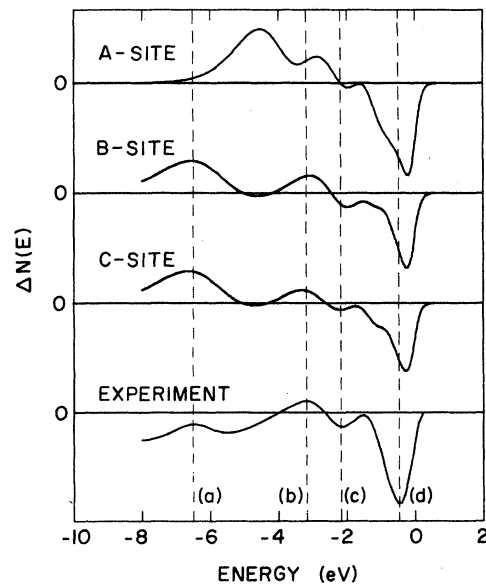


FIG. 4. Comparison of the calculated H-induced photoemission difference spectra with the experimental difference curve. The experimental curve is from Fig. 2 of Ref. 4.

ment, the theoretical difference spectrum

$$\Delta N(E) = \sum_i \int_{-\infty}^{E_F} \Delta n_i(E') f(E - E', \gamma(E)) dE' \quad (1)$$

is constructed, where  $\Delta n_i$  is the difference between the local DOS of the chemisorbed surface and that of the clean surface for the  $i$ th layer;  $f(E - E', \gamma(E))$ , a lifetime and instrument broadening factor, is a Gaussian function with an energy-dependent width. [The full width at half maximum is given by the empirical relation<sup>13</sup>  $\gamma(E) = 0.15|E - E_F| + 0.2$  eV.] Equation (1) thus approximates the changes in the photoemission intensities in angle-integrated measurements if final-state and matrix-element effects are neglected. The theoretical  $\Delta N(E)$  for the three chemisorption geometries is presented in Fig. 4 together with the experimental  $\Delta N(E)$  from Ref. 4. All three theoretical curves are obtained with *no* adjustable parameters and are found to be not very sensitive to small deviations in the H-Pd interplanar distance.<sup>14</sup>

Of the four main features in the experimental data, the structure [labeled (d)] just below  $E_F$  is reproduced in all three theoretical spectra. These results confirm a previous interpretation by the author<sup>6</sup> that the characteristic adsorbate-induced reductions of the photoemission intensity at energies near  $E_F$  are due to changes in the surface density of states. Because these changes are brought about by the removal (bonding away to lower energies) of surface states and resonances, they are not very sensitive to the nature of the adsorbate or to its position. From Fig. 4, site A can be immediately ruled out as the preferred site since the prominent experimental H-induced feature at  $-6.5$  eV (arising from the bonding H-Pd band) is shifted upward by  $\sim 2$  eV toward  $E_F$ . The spectra for sites B and C, on the other hand, reproduce remarkably well the experimental spectrum with regard to both the peak positions and their general shapes. The agreement is slightly better for site C in the region of the Pd  $d$ -band complex. However, the approximations used in evaluating  $\Delta N(E)$  and the uncertainties in the experiment<sup>15</sup> prevent a discrimination between the two threefold sites B and C. But, since their surface band structures are virtually identical, the interpretation of the experimental

features is the same for both geometries. The origin of the remaining two features in the experimental spectrum is the following. The peak at  $-3.2$  eV arises mainly from the appearance of the two surface bands in the gap in the PBS near  $\bar{\Gamma}$ . (See Fig. 1.) Correspondingly, the valley at  $-2.2$  eV results from the removal of the above-mentioned surface states and of the surface states about  $\bar{K}$  from this energy region.

It is a pleasure to thank J. E. Demuth, D. E. Eastman, and A. R. Williams for valuable discussions.

<sup>1</sup>B. I. Lundqvist, H. Hjelmberg, and O. Gunnarsson, in *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher *et al.* (Wiley, London, 1978). This is an excellent review with extensive up-to-date references.

<sup>2</sup>H. Conrad, G. Ertl, and E. E. Latta, *Surf. Sci.* **41**, 435 (1974).

<sup>3</sup>There are two other existing self-consistent calculations on adsorbates on  $d$ -band metal films: Non three layers of Cu(100) [J. R. Smith, F. J. Arlinghaus, and J. G. Gay, *Solid State Commun.* **24**, 279 (1977)] and O on three layers of Ni(001) (C. S. Wang and A. J. Freeman, to be published).

<sup>4</sup>J. E. Demuth, *Surf. Sci.* **65**, 369 (1977).

<sup>5</sup>H. Conrad, G. Ertl, J. Kupperts, and E. E. Latta, *Surf. Sci.* **58**, 578 (1976).

<sup>6</sup>S. G. Louie, *Phys. Rev. Lett.* **40**, 1525 (1978).

<sup>7</sup>S. G. Louie, K.-M. Ho, and M. L. Cohen, *Phys. Rev. B* (to be published).

<sup>8</sup>K.-M. Ho, M. L. Cohen, and M. Schlüter, *Phys. Rev. B* **15**, 3999 (1977).

<sup>9</sup>The eigenvalues are convergent to within 0.15 eV of those obtained from a basis set which contains twice the number of plane waves.

<sup>10</sup>K. H. Johnson, *Int. J. Quantum Chem.* **11**, 39 (1977), and references therein.

<sup>11</sup>D. E. Eastman, J. K. Cashion, and A. C. Switendick, *Phys. Rev. Lett.* **27**, 35 (1971); A. R. Williams, J. Kubler, and C. D. Gelatt, Jr., to be published.

<sup>12</sup>D. M. News, *Phys. Rev.* **178**, 1123 (1959); K. Schönhammer, *Solid State Commun.* **22**, 51 (1977).

<sup>13</sup>F. J. Himpsel, private communication.

<sup>14</sup>E.g., a 15% change in the H-Pd interplanar distance for site C results in  $< 0.1$  eV change in the position of peak (a) in Fig. 4.

<sup>15</sup>Photoemission structures in the  $d$ -band complex are dependent on photon energy due to matrix-element and final-state effects.