Linear Combination of Atomic Orbitals Model for the Electronic Structure of H₂ on the W(001) Surface

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The electronic structure of both the bare W(001) surface and one with a saturation coverage of H atoms has been calculated for a sixteen-layer slab using a parametrized linear combination of atomic orbitals (LCAO) model. The results permit an identification of H-induced structures that have been observed in recent angle-resolved photoemission experiments.

Although the saturation adsorption of H_2 on W(001) is one of the most studied systems in surface physics, its electronic structure is far from well understood.[1] Recent angle-resolved photoemission studies[2,3] on this system, however, appear to be providing incisive experimental information from which one should, in principle, be able to deduce its electronic structure. The key feature of these measurements is that they determine the energy versus parallel wave-vector (E vs $\vec{k}_\parallel$) relations for the H-induced structures in the spectra. We describe here the results of a LCAO model calculation which is intended as the theoretical counterpart of the angle-resolved photoemission work. We show that the E vs $\vec{k}_\parallel$ relations of prominent surface states/resonances in the calculations bear a strong resemblance to the experimental dispersion relations, and therefore permit some tentative identifications. These depart appreciably from previous interpretations. We believe that this represents the first attempt to use the LCAO technique in a detailed analysis of angle-resolved photoemission on a chemisorption system.

The model consists of a sixteen-layer slab of W atoms with H atoms on one or both sides of the slab located in the bridge positions in accordance with the Estrup-Anderson model.[4] The Slater-Koster LCAO Hamiltonian for the slab was set up in the standard way.[5] We used nine orbitals for W (for $6s$, $6p$, and $5d$) and a single $1s$ orbital for each of the two H atoms in the unit cell. The W-W LCAO interaction parameters were obtained by a fit to nonrelativistic augmented-plane-wave (APW) calculations of the bulk W band structure. The fit was performed by Chakraborty, Pickett, and Allen[6] by using a procedure employed earlier on Nb and Mo. The W-H and H-H interaction parameters were obtained by the following artifice. An APW calculation was performed for a fictitious tungsten hydride crystal having the CsCl structure and a W-H bond distance of 2.14 Å. An

LCAO fit to the APW results then provided values for the W-H and H-H interaction parameters. We then assumed that these bulk parameters were *transferable* to a treatment of the surface situation. Up to this point, the parameters are determined entirely from the results of first-principles calculations. We then made a single empirical adjustment, that of lowering the center of gravity of the H $1s$ levels so that the hydrogen $1s$ band was essentially half filled.

The results for the two-dimensional energy bands of the bare W(001) surface are displayed in Fig. 1 for two principal symmetry directions. We
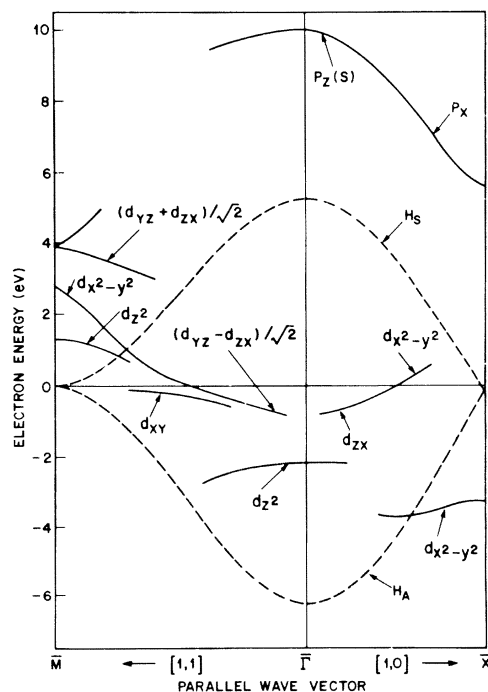

FIG. 1. Two-dimensional band structure for the prominent surface states/resonances on the bare W(001) surface. The bands are labeled with the principal orbital content in the LCAO eigenvector. The dashed curves represent the band structure for an isolated sheet of H atoms.

show here only the most prominent surface states
and resonances; by this, we mean those states
whose eigenvector components are conspicuously
large in the outermost atomic layer(s). From
here on, we will make no distinction between sur-
face states and surface resonances, and simply
refer to both as surface states. Each of these
states has been labeled with the W orbital which
has the largest amplitude in the LCAO eigenvec-
tor. In some cases, this varies with position in
k space. For example, in the range between -1
eV and the Fermi energy E_F, there is a state in
the $[1,0]$ direction whose largest component is of
d_{zx} character while close to Γ. This state also
has a large $d_{x^2-y^2}$ component which becomes pre-
dominant on moving away from Γ. We identify
this particular surface state with the state ob-
served by Feuerbacher and co-workers.[7,8] The
sense of the dispersion agrees with the experi-
ments, although the absolute energy differs by
about 0.5 eV. Note that since our model is non-
relativistic, the existence of a surface-state fea-
ture in this energy range does not necessarily re-
quire the existence of a spin-orbit gap,[9] a result
in agreement with the conclusions of other work-
ers.[10]

The dashed curves in Fig. 1 represent the H-H
band structure (i.e., the electronic states for the
sheet of H atoms in which the H-H interaction
parameters are kept "on" but where the W-H in-
teraction parameters are switched off). As men-
tioned above, the center of gravity of the H-H
bands has been adjusted so as to coincide quite
closely with E_F. The center of gravity obtained
directly from the LCAO fit to fictitious WH was
well above E_F and, in the surface situation, would
have implied an unphysically large transfer of
charge from the H atoms to the W substrate. The
nearest-neighbor H-H interaction parameter ob-
tained from this LCAO fit turns out to be positive
(i.e., repulsive). This means that the antisym-
metric combination of $1s$ orbitals on the two H
atoms in the unit cell has a lower energy than the
symmetric combination. The lower (upper) H-H
band in Fig. 1 designated H_A (H_S) involves the an-
tisymmetric (symmetric) combination of H $1s$ or-
bitals.

The numerical results for a saturation cover-
age of H_2 on W(001) are shown in Fig. 2. These
results and those of Fig. 1 were actually obtained
in a single calculation for a sixteen-layer W slab
with H atoms on both sides. On one side, the W-
H interactions were switched off corresponding
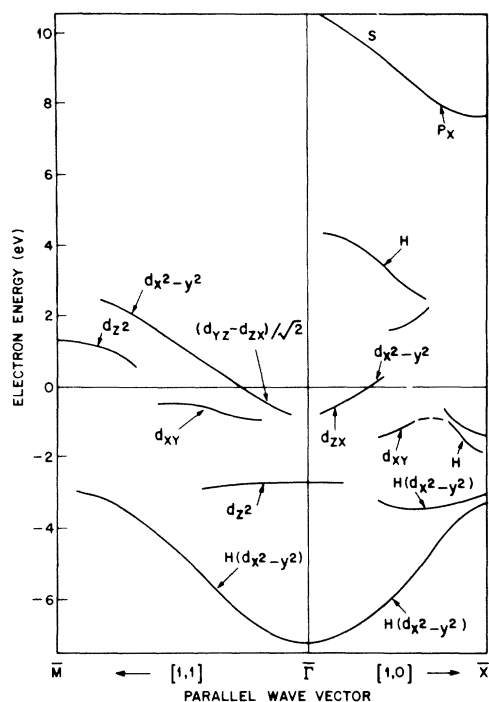to the bare W(001) states and H-H band-structure

FIG. 2. Two-dimensional band structure for the sur-
face states/resonances on a W(001) surface with a satu-
ration coverage of H atoms located at the bridge sites
of the Estrup-Anderson model.

results of Fig. 1. On the other side, the W-H in-
teractions were switched on, giving rise to the
results of Fig. 2. As in Fig. 1, the states in Fig.
2 have been labeled according to the principal or-
bital content. The states whose principal orbital
content is hydrogen $1s$ have been labeled H, with
the largest W orbital content following in paren-
theses where appropriate.

We now attempt to identify these calculated
states with the H-induced structures reported by
Feuerbacher and Willis.[2] The experimental re-
sults of Ref. 2 are plotted in Fig. 3. The full
curves (A, B, etc.) represent the positions of the
centers of rather broad (width ~ 1 eV) resonances.
We have deviated in one respect from the original
assignments of Feuerbacher and Willis in that we
have chosen to assign the experimental structures
observed at apparent energy of about -12 eV to
the unoccupied region. These structures are la-
beled F and G in Fig. 3.

The strongest H-induced resonance in the data
of Ref. 2 occurs at $\overline{\Gamma}$ in the energy range -2 to
-3 eV and is labeled C in Fig. 3. We identify
this resonance with the state of d_{z^2} symmetry in
this energy range shown in Fig. 2. This state is
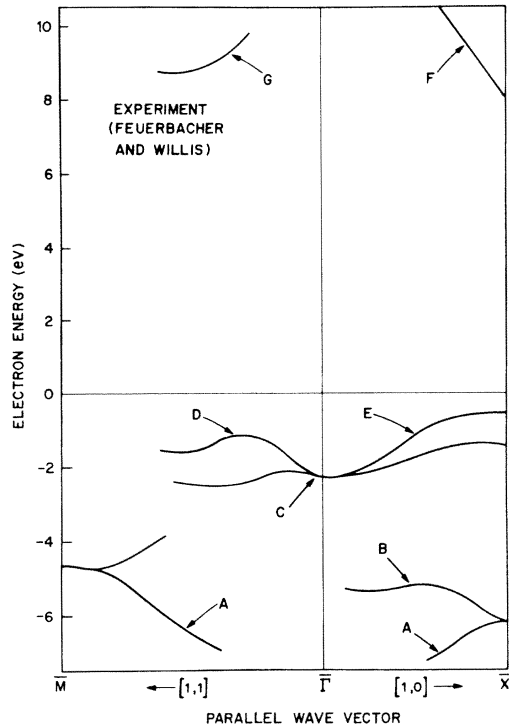clearly related to the d_{z^2} surface state on the bare

FIG. 3. Experimental results from Ref. 2 for the E vs $\vec{k}_\parallel$ dispersion of the hydrogen-induced resonances in photoemission spectra from a W(001) surface covered with a saturation adlayer of hydrogen. The photon energy was 21.2 eV.

W(001) surface. After H adsorption, this state is shifted slightly in energy and picks up a small but significant amount of H(1s) content (antisymmetric combination within the unit cell). Note that since d_{z^2} is of e_g symmetry, our interpretation differs from that in Ref. 2 where this resonance is associated with the t_{2g}-like $\Gamma_{25'}$ levels of the bulk band structure.

The H-induced structures labeled A in Fig. 3 are identified here with the H-based band in Fig. 2 which occurs at an energy of about -7 eV at $\bar{\Gamma}$ and has upwards dispersion on moving away from $\bar{\Gamma}$. The sense of this dispersion is in agreement with experiment. At $\bar{X}$, this calculated band is almost degenerate with a rather flat band whose energy is at about -3.4 eV. This is rather similar to the behavior of the experimental structure labeled B, except that the experimental structure occurs closer to -5 eV. Note that the main W orbital content in these lower-energy structures is $d_{x^2-y^2}$. Our interpretation therefore differs from that of Egelhoff and Perry[3] who, on the basis of of extended Hückel calculations by Anders, Hansen, and Bartell,[11] attribute the lowest structure

to binding with the W 6s orbital.

Our calculations do not reproduce the H-induced structures at an apparent energy of -12 eV reported in Ref. 2. As indicated above, we have assigned these structures (labeled F and G in Fig. 3) to the unoccupied region and we identify F with the surface state based on the W p orbitals shown in Fig. 2. This is in the correct final-state energy range and has a dispersion (downward in energy away from $\bar{\Gamma}$) in agreement with experiment.

The theoretical features with which we are identifying the H-induced experimental photoemission structures are of two kinds. In one kind, the surface states have primarily H 1s orbital content. The other kind consists of H-induced modifications of states which already exist on the bare W(001) surface. The question then arises as to why the states of this latter kind (e.g., the d_{z^2} state between -2 and -3 eV) are observable only after adsorption. We conjecture that emission from these states is inhibited by small optical momentum matrix elements before adsorption, but the small admixture of H 1s orbital content after adsorption leads to a stronger matrix element and permits the state to assert itself strongly in the measured photoemission spectrum.

In conclusion, we have demonstrated the utility of the LCAO two-dimensional band-structure approach in the detailed analysis of angle-resolved photoemission data for the saturation converage of H_2 on W(100). It should be recognized that these results are preliminary in nature. Both the qualitative and quantitative details are found to be sensitive to the choice of LCAO parameters. The positive sign for the H-H interaction, for example, has a strong qualitative effect on the form of the results. What does seem clear is that inclusion of the H-H interactions is essential, and that interpretations based on surface molecules or cluster calculations using only a single H atom will not be adequate for this particular system.

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Orientation of CO on Pt(111) and Ni(111) Surfaces from Angle-Resolved Photoemission*

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Angle-resolved photoemission spectra of the molecular orbitals of chemisorbed CO on Pt(111) and Ni(111) substrates show a strong angular variation of the peak intensity ratio. Comparison with Davenport's $X\alpha$ calculations establishes that CO stands up on these substrates, with the carbon atom bonded to the substrate. The Pt $5d(t_{2g})$ orbitals are found to be strongly involved in chemisorption bonding to CO.

The interaction of chemisorbed adsorbate molecules with catalytically active substrates has formed the focus of much recent research activity in surface physics. Because of the importance of the CO/Pt and CO/Ni systems in heterogeneous catalysis for synthesis of hydrocarbons, these systems have served as prototypes for surface studies. Until now, however, no firm evidence has been presented regarding the orientation of absorbate CO molecules on crystalline nickel or platinum surfaces.

Davenport[1] presented SW $X\alpha$ calculations of photoelectron angular distributions from the molecular orbitals of oriented CO molecules and pointed out that chemisorbed CO should display similar angular distributions provided that the molecular wave functions are not strongly perturbed by the substrate. In this Letter, we report photoelectron angular distributions from CO adsorbed on both Pt(111) and Ni(111) surfaces. These data provide the first definitive evidence that the CO molecules "stand up" in both cases, with the carbon atoms bonded to the substrate. Furthermore, the spectra clearly show that the t_{2g} orbitals of the Pt $5d$ band are strongly involved in the Pt-C chemisorption bond. The experiments reported here were carried out with conventional photoemission equipment (He lamp, cylindrical mirror analyzer) and thus point out the potential of such studies to determine bonding geometries. It is

clear that by making use of variable-energy, highly polarized synchrotron radiation, such studies become even more powerful.

Experiments were carried out using the $h\nu$ = 40.8 eV radiation emitted by a He II resonance lamp. Single crystals of Pt and Ni were cut along the (111) planes and cleaned *in situ* under ultra-high-vacuum conditions. In the case of Pt, it was necessary to alternate periods of Ar^+ bombardment of the specimen at 950°C and oxidation in an atmosphere of 10^{-5} Torr O_2 at 850°C for two weeks in order to remove calcium and carbon impurities diffusing to the crystal surface from the bulk. Nickel was cleaned by repeated Ar^+ bombardment and annealing. The photoemission studies were conducted at a background pressure of impurities (other than He) less than 8×10^{-11} Torr. In the angle-dependent studies, both the unpolarized photon beam and the propagation direction of the analyzed electrons were in a horizontal plane, and the crystal could be rotated about a vertical axis in the plane of the (111) surface. Angle-resolved photoemission (ARP) was facilitated by masking all but an 11° arc of a cylindrical mirror analyzer, yielding an effective angular resolution of $(5 \pm 1)°$ half-angle.[2] Figure 1 shows the variation of the clean valence-band spectra (solid line) and the corresponding spectra after adsorption of ~ 4 L CO (dotted line), plotted against θ, the angle of rotation from the