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Electronic structure of hydrogen and oxygen chemisorbed on plutonium: Theoretical studies

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The film linearized-muffin-tin-orbital method has been used to calculate the electronic structure of hydrogen and oxygen chemisorbed on plutonium. The calculated work functions are larger than that obtained for a clean Pu surface. This suggests that a change in the surface dipole moment is induced by the chemisorbed H and O atoms. For the H chemisorbed state it is found that the fourfold-bridging position is stable with regard to motion out of or into the plutonium surface plane—with only a small relaxation effect, and that the energy gained when the H atoms chemisorb on the Pu surface is 4.0 eV per atom. The localized, spin-polarized $5f$ electrons in PuH_2 are found to induce a substantial conduction-band moment. The calculations suggest that the electronic structure of the oxygen chemisorbed state is more covalent than the hydrogen chemisorbed state.

I. INTRODUCTION

Recently it has become possible to calculate the electronic structure and related properties of surfaces to high accuracy. This has been shown in a number of theoretical investigations using, for instance, the film linear-muffin-tin-orbital method[1] (FLMTO) and the full-potential linear augmented-plane-wave method (FLAPW).[2] These calculational methods have given results that very accurately account for experimental data such as work functions, angular-resolved photoemission intensities, and magnetic properties. We have recently extended such FLMTO calculations to the plutonium surface.[3] Therefore it is now possible reliably to treat systems for which it is difficult to obtain experimental data, within a theoretical framework. The plutonium surface is a typical system where experimental work has been difficult due to material problems. The present work has been motivated by the chemisorption of hydrogen and oxygen on plutonium. Although the experimental data are quite sparse, some investigations have been performed. It was found that initially when Pu is exposed to O, a dioxide layer is formed at the surface. This dioxide layer was detected to have the CaF_2 structure, which is the same structure found in bulk PuO_2.[4] No experimental studies of hydrogen chemisorption on plutonium have been published to our knowledge. However, plutonium is known to adsorb hydrogen strongly[5] and the PuH_2 compound is stable. Therefore, considering the oxygen chemisorption behavior, we assume that for hydrogen chemisorption a PuH_2 layer is formed at the surface and the calculations were performed making this assumption. The H and O chemisorbed states can therefore be viewed as the surface states of the PuH_2 and PuO_2 compounds (both CaF_2 structure).

Plutonium dihydride has a localized $5f$ shell with a trivalent Pu ion (Pu^{3+}). This can be understood from the fact that the interactinide distances in the compound are larger than in Pu metal, so that the $5f$ overlap is reduced, and the $5f$ states become localized. PuH_2 was shown to have trivalent Pu ions, from x-ray photoelectron spectroscopy data, which yield a $4f$ intensity at the same energies as for[6] Pu_2O_3. Neutron-scattering data[7] yield a moment of $0.71\mu_B$ which is the same as the trivalent free ion value. Nuclear-magnetic-resonance measurements[8] are also in agreement with a trivalent configuration. The resistivity of the compound[6] is considerably higher than that of the pure metal (α-Pu). Early susceptibility and specific-heat measurements indicated an antiferromagnetic[9] ordering. However, more recent experiments showed that PuH_2 is a ferromagnet.[6] Susceptibility data[6,9] indicate that the effective (paramagnetic) Bohr magneton number is close to the free ion value ($P_{\text{eff}}=0.96\mu_B$), and neutron scattering gives an ordered moment of $0.71\mu_B$.[7] However, the magnetization measurements[6] show a smaller value of the ordered moment (about $0.5\mu_B$) compared to the free ion value ($0.71\mu_B$). A part of the motivation for this work is this measured discrepancy.

Contrary to PuH_2, it was found from susceptibility and specific-heat measurements that no magnetic transition takes place in PuO_2.[10] This was explained by the tetravalent (Pu^{4+}) state of the Pu ion in PuO_2 which gives rise to a singlet ground state.[11] Furthermore, it was found that PuO_2 shows typical oxide semiconducting properties.[12]

II. DETAILS OF THE CALCULATIONS

The calculations were performed using the FLMTO method,[1] using a slab geometry (containing three Pu layers) with periodicity in two dimensions. Space is divided into muffin-tin sphere and interstitial regions inside the slab and a region outside (the vacuum). The basis functions are muffin-tin orbitals[13] together with plane-wave orbitals,[1] i.e., functions that behave like two-dimensional plane waves in the direction parallel to the surface. In the direction perpendicular to the surface, the plane-wave orbitals are solutions to the planar averaged potential in the vacuum region. Inside the slab the plane-wave orbitals have plane-wave-like behavior or a real exponential behavior depending on the k point, reciprocal-lattice vector, and the energy parameter. The full potential is used everywhere except inside the muffin-tin spheres where the non-muffin-tin (NMT) potential is approximated by the extended NMT potential.[1] The exchange-correlation potential was generated from the charge density using the Vosko-Wilk-Nusair parametrization[14] of the local-spin-density approximation. The eigenvalues were calculated at ten special k points in the irreducible wedge of the two-dimensional Brillouin zone. All scalar relativistic calculations were assumed to be self-consistent when the total energy was stable to the order of 0.1 mRy.

The slab geometry was chosen to have the CaF_2 structure for the "bulk" atoms (the Pu atoms are positioned on a fcc sublattice in this structure [Fig. 1(a)]). The atomic positions of the bulk atoms were therefore (0,0,0) for Pu and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(-\frac{1}{4},-\frac{1}{4},-\frac{1}{4})$ for H. For the Pu atoms at the surface the positions were also assumed to have the CaF_2 geometry. However, the chemisorbed atoms (H and O) were assumed to have the fourfold-bridging position at the surface [Fig. 1(b)]. Since the $5f$ electrons are known to be localized in these compounds we have treated them as core states. The main motiva-

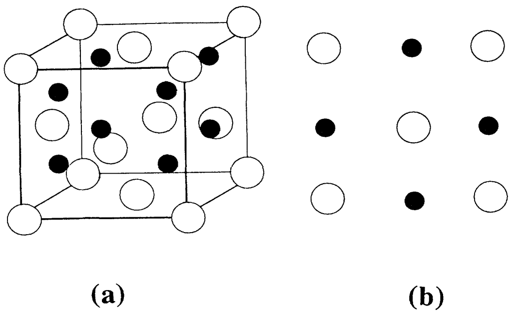

FIG. 1. (a) The crystal structure of bulk PuH_2 and PuO_2. The Pu atoms are indicated by ○, whereas the H and O atoms are indicated by ●. (b) The atomic arrangement on the surface of PuH_2 and PuO_2 (top view). ○, the Pu atom, and ●, the H and O atoms.

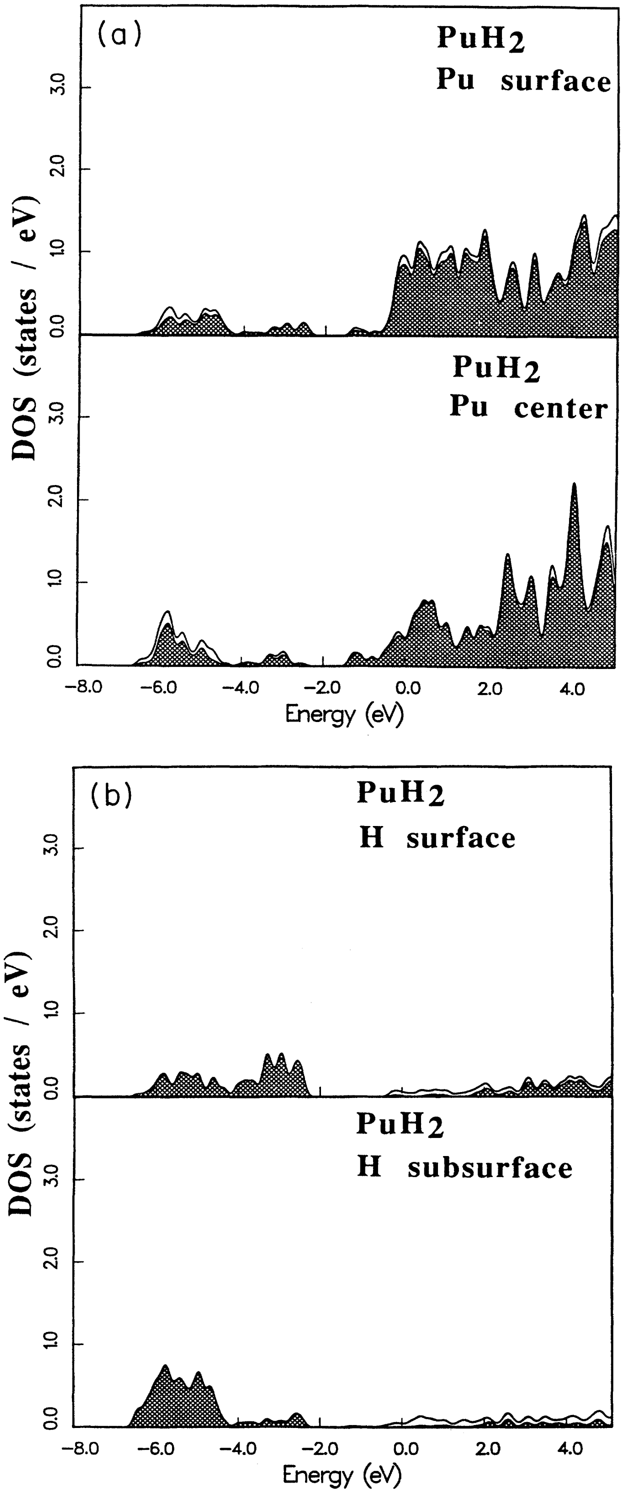

FIG. 2. The Pu-projected (a) and H-projected (b) DOS from the paramagnetic calculation for PuH_2. The upper panel shows the sphere-projected DOS for the surface atom, and the bottom panel shows the sphere-projected DOS for the bulk atom. Energies are in electron volts, and the Fermi level is at zero. The cross-hatched area indicates the Pu $6d$ (a) and the H $1s$ (b) partial DOS.

TABLE I. Orbital projected occupation numbers and work functions for the paramagnetic calculations.

	PuH_2		PuO_2	
	Bulk	Surface	Bulk	Surface
Pu				
n_s	0.077	0.063	0.120	0.084
n_p	0.116	0.081	0.172	0.106
n_d	0.645	0.689	0.814	0.761
Ligand				
n_s	0.975	0.777	0.013	0.010
n_p	0.044	0.038	3.866	3.617
n_d	0.057	0.053	0.012	0.008
Interstitial charge[a]	6.051		9.623	
Vacuum charge	0.405		0.535	
Work function (eV)	4.4		4.8	

[a] Interstitial charge for 9 atoms per unit cell.

tion for this work is the study of chemisorption of H and O on the Pu surface. However, since the 5f electrons are magnetically polarized in PuH_2, we therefore, out of necessity and interest, study the magnetic properties of this system as well. However, the spin polarization of the chemically inert 5f electrons is not expected to influence the chemical bonding and therefore not to modify the physical properties of the chemisorbed state. The unit cell contained 9 atoms (3 Pu and 6 H or O); and with 9 muffin-tin orbitals per atom we used 81 muffin-tin orbitals together with 14 plane-wave orbitals in our calculations. The core states were recalculated at each iterative step by solving the Dirac, or the spin-polarized Dirac equation.

III. RESULTS

The self-consistently calculated density of states (DOS) of paramagnetic PuH_2 is shown in Fig. 2. Notice that the DOS for the Pu atoms is dominated by the 6d orbitals [Fig. 2(a)]. The H atoms have, as expected, mostly 1s states [Fig. 2(b)]. These Pu 6d and H 1s states hybridize strongly and give rise to a broad band starting about 7 eV below the Fermi level (E_F). Furthermore the Pu 6d orbitals are found to have their main weight at energies at and above E_F, whereas the H 1s states are centered at about 6 eV below E_F. A natural question that arises is whether the H atoms accept (donate) an electron to produce a full (empty) shell. However, as suggested from the occupation numbers (Table I) there is little charge transfer between the H and Pu atoms. Summing the H charge occupation numbers in Table I gives an average occupation of about 1.01 electrons per H atom. Notice that the "bulk" H atoms have slightly larger occupation than the surface atoms, which "leak" some electrons to the vacuum. The Pu atoms are seen to lose an appreciable amount of charge, mainly to the interstitial region (Table I). This is a reflection of covalent character in the bonding. However, we point out that the charge occupation numbers should not be treated as unique, since they to some extent depend on the choice of the muffin-tin radii. Instead of ionic bonding, with large charge transfer between the different atoms in the unit cell, hybridization between the H 1s and Pu 6d states is the dominating feature. Therefore the bonds in PuH_2 have appreciable covalent character. This was also found in the calculation of bulk PuH_2.[15]

Similar behavior is found for the electronic structure of PuO_2, namely that the Pu projected DOS is dominated by the 6d orbitals [Fig. 3(a)]. The 2p states dominate the O projected DOS [Fig. 3(b)], and it is the Pu 6d–O 2p mixing that dominates the hybridization. We also find, in agreement with experimental data, that this system is a semiconductor. For PuO_2 also, there is little charge transfer between the different atom types (Table I). Notice that the charge inside the O muffin-tin radius is close to 4 and that the O atoms therefore are more or less charge neutral. Note also that although the Pu atoms are tetravalent in PuO_2, the charge occupation numbers inside the Pu muffin-tin sphere are quite close to the values found for PuH_2. Therefore, the extra valence electron in PuO_2 is in the interstitial charge. The two systems therefore differ quite substantially in that PuO_2 has *more charge in the interstitial region,* yielding an even *more pronounced covalent character* of the chemical bonding. Furthermore, it is seen from Fig. 3 that the O 2p states in PuO_2 are broader than the H 1s states in PuH_2. However, it is difficult to notice any substantial narrowing of the surface states as compared to the bulk ones, both in PuH_2 and PuO_2.

Turning to the charge density of PuH_2 we notice (Fig. 4) that the hydrogen atoms have an oval-shaped density, with a tendency to pile up charge between the H atoms. The charge density associated with the Pu atom is even less spherical and extends more in space. This is seen in the spacing between dotted contours (found around the Pu atom) which is smaller than between the solid ones (found around the H atom). Furthermore, it can be seen from Fig. 4 that there is a substantial amount of charge in the interstitial region (this can also be seen in Table I). To some extent the interstitial charge density piles up between the atoms. Therefore, the bonding has some covalent character in PuH_2. The charge density of PuO_2 is found to be spherically symmetric around the O atoms (Fig. 5), whereas the charge density of the Pu atom is

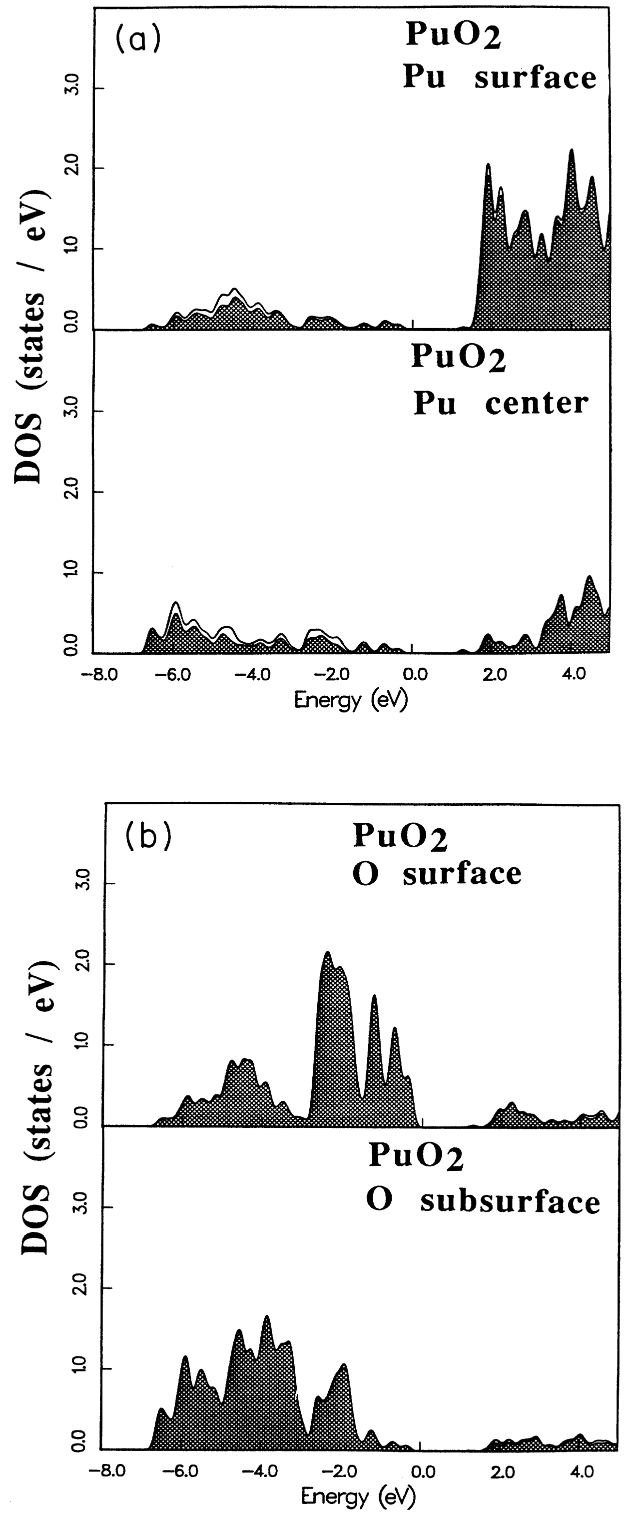

FIG. 3. The Pu-projected (a) and O-projected (b) DOS from the paramagnetic calculation for PuO_2. The upper panel shows the sphere-projected DOS for the surface atom, and the bottom panel shows the sphere-projected DOS for the bulk atom. Energies are in electron volts, and the Fermi level is at zero. The cross-hatched area indicates the Pu 6*d* (a) and the O 2*p* (b) partial DOS.

more extended in space. Here parts of the charge density pile up between the atoms making the bonding even more covalent than in PuH_2. Finally, notice that both for PuH_2 and PuO_2 at distances far away from the surface, the charge density is more or less flat with little variation horizontally to the surface plane.

The calculated work functions are 4.4 and 4.8 eV for PuH_2 and PuO_2, respectively, and are larger than what we have obtained previously for the clean Pu(001) surface (3.7 eV).[3] This implies that the chemisorption of H and O induces an increase in the surface dipole moment. Clearly the O chemisorbed state induces a larger dipole moment, since the change in work function from the clean Pu surface is larger for this system.

We have also calculated the total energy as a function of the distance between the H atom and the surface plane (both inward as well as outward displacement from the plane) and found that the total energy is minimized when the H atoms are moved out 0.01 Å from the surface plane. This is a very small relaxation effect, and all calculated properties such as work function and occupation numbers are very little affected by this relaxation. The difference between the total energy of the chemisorbed state and the state with the H atom at infinity gives the energy of chemisorption, and it is 4.0 eV per atom.

IV. SPIN-POLARIZED RESULTS

Although the main motivation for this work is the chemisorption of H and O on Pu, we have also performed a spin-polarized calculation letting the localized-polarized core electrons induce a moment in the conduction band. The PuH_2 system is know to have localized 5*f* electrons with a magnetic moment close to the free-ion (Pu^{3+}) value.[6,7,9] These polarized electrons will induce a conduction-band moment, and we have performed spin-polarized calculations to investigate this in more detail. For simplicity this was done using the unrelaxed geometry. We do not anticipate that the magnetic properties will be affected by a 0.01-Å relaxation. The spin component of the total 5*f* moment (which is coupled antiparallel to the total 5*f* moment) can be obtained using the vector equality $\langle s_z \rangle = (g_J - 1)J$. One obtains from this expression a 5*f* spin moment of $3.57\mu_B$. This moment has been used as the spin configuration for the five localized 5*f* electrons in our spin-polarized calculations. Thus we have calculated the valence and core states self-consistently using this spin configuration for the localized 5*f* states. The core states were calculated at each iteration by solving the spin-polarized Dirac[16] equation. The core spin and charge density polarize the conduction band. The occupation numbers and magnetic moments are shown in Table II. Note that the induced moments of the valence states are significant. Note also that the induced spin moment for the Pu atom at the surface is larger than for the bulk atom ($0.08\mu_B$ for the Pu atoms in the bulk and $0.14\mu_B$ for the Pu atoms at the surface). Since an appreciable amount of charge is found in the interstitial region, a fairly large spin moment is also found there. The results indicate that the conduction-band polarization is about $0.22\mu_B$ per Pu atom. Due to hybridi-

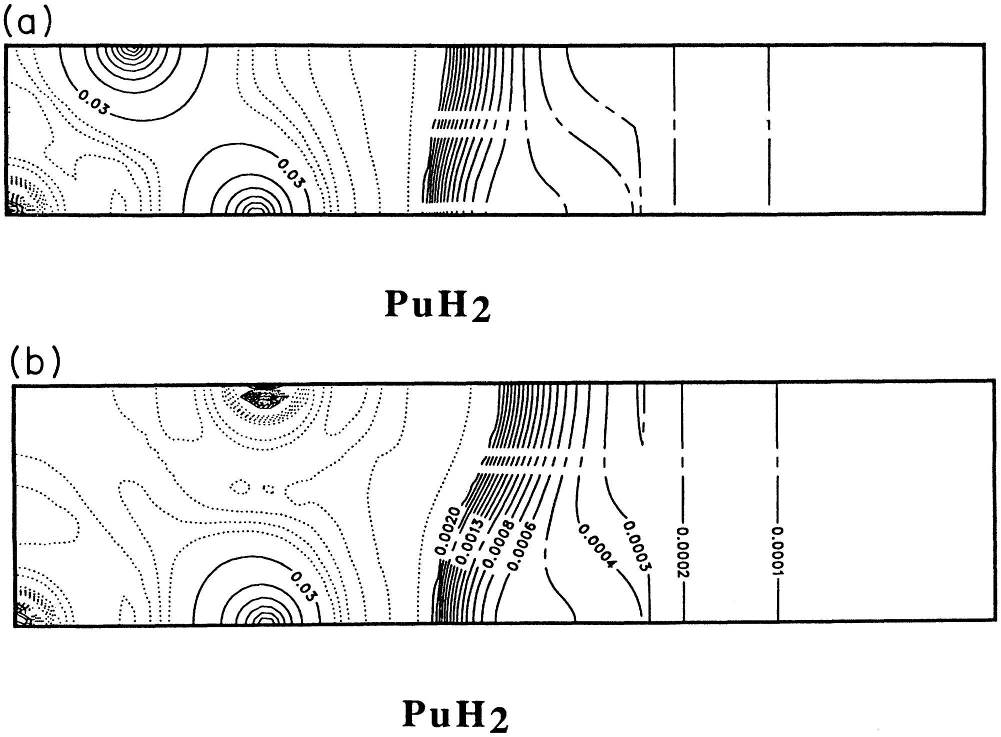

FIG. 4. Charge-density contour map (in electrons/a.u.^{3}) for PuH_2 cut along the [110] direction (a) and the [100] direction (b). The spacing between the solid lines is 0.01, between the dotted lines 0.003, and between the dashed lines 0.0001.

zation effects this in turn polarizes the H atoms so that their spins are antiparallel to the Pu atoms. However, the spin moments for the H atoms are very small. The coupling between spin moments in compounds has previously been investigated in detail[17] and was found to be caused by hybridization effects.

The induced conduction-band polarization reduces the total moment (since the spin and total moments are antiparallel) and offers an explanation for the unusually low value found for the total (ordered) moment. Namely, from the susceptibility measurements it is known that the effective Bohr magneton number is close to the free-ion value. The free-ion value of the total moment is $0.71\mu_B$, and this is the ordered moment measured by neutron scattering (which essentially measures the $5f$ core moment), but the total moment found by magnetization measurements is about $0.5\mu_B$.[6] If we subtract our calculated conduction-band moment from the value reported by neutrons[7] $(0.71\mu_B)$ we obtain a total (ordered) moment which is close to the experimental value. The work func-

TABLE II. Orbital projected occupation numbers, magnetic moments, and work function for the spin-polarized calculation of PuH_2.

	Bulk			Surface		
	n_s	n_p	n_d	n_s	n_p	n_d
Pu(up)	0.039	0.054	0.372	0.034	0.039	0.439
Pu(down)	0.037	0.055	0.288	0.030	0.038	0.303
H(up)	0.473	0.025	0.003	0.379	0.021	0.003
H(down)	0.490	0.018	0.002	0.399	0.017	0.003
spin moment (μ_B)	m_s	m_p	m_d	m_s	m_p	m_d
Pu	0.002	−0.001	0.084	0.004	0.001	0.136
H	−0.017	0.007	0.001	−0.020	0.004	0.000
Interstitial						
Moment[a] (μ_B)		0.3				
Work function (eV)		4.5				

[a] Interstitial moment for 9 atoms per unit cell.

tion for the spin-polarized calculation is 4.5 eV and differs very little from the paramagnetic calculation (as do other properties, for instance, occupation numbers) and shows that the spin polarization of the chemically inert $5f$ electrons does not affect the physical properties of the chemisorbed system.

In Fig. 6 the valence spin density obtained from the spin-polarized calculation is shown. Notice that the magnitude of the spin density is appreciable at the atomic sites and is to a large extent spherically symmetric. However, for the spin density cut along the [110] direction a region of positive spin density is seen extending out from the H atom towards the vacuum region. This feature is explained by the induced polarization due to the two Pu atoms sitting above this H atom. The spin density around the H atom is found to be negative, i.e., opposite to the moment of the Pu atom. As mentioned above, this is a reflection of hybridization effects.[17]

The DOS from the spin-polarized calculation (not shown) is very similar to the paramagnetic DOS. However, the spin-up states are shifted downwards and the spin-down states are shifted upwards, more or less rigidly. The spin splitting of the valence states emanates from the difference in spin-up and spin-down potentials generated by the polarized $5f$ electrons.

To get a simple understanding of the induced spin splitting of the valence band, we proceed with a model calculation based on the work presented in Ref. 18. It has been shown that the change in total energy due to the spin polarization of a system can be written as[18]

$$E=\frac{1}{4}\sum_{l,l'} m_l I_{l,l'} m_{l'} \ . \tag{1}$$

Here $I_{l,l'}$ is the exchange integral and m_l is the magnetic moment associated with orbital l. Differentiating this expression with respect to $m_{l''}$ gives a splitting between the spin-up and spin-down states of the orbital l'' which can be written as

$$\Delta E_{l''}=\sum_{l} m_l I_{l,l''} \ . \tag{2}$$

In our case l'' is the Pu $6d$ orbital and the only other state carrying an appreciable moment is the $5f$ orbital. Hence the splitting of the $6d$ states can be written as $\Delta E_{6d}=m_{5f}I_{5f\,6d}$. $I_{5f\,6d}$ has been calculated to be 0.12 eV.[18] Therefore, with $m_f=3.57\mu_B$ we obtain a splitting between the spin-up and spin-down states of about 0.4 eV. This value compares well with the fully self-consistent one (examining the splitting of the eigenvalues that mostly have $6d$ character) and gives a simple under-

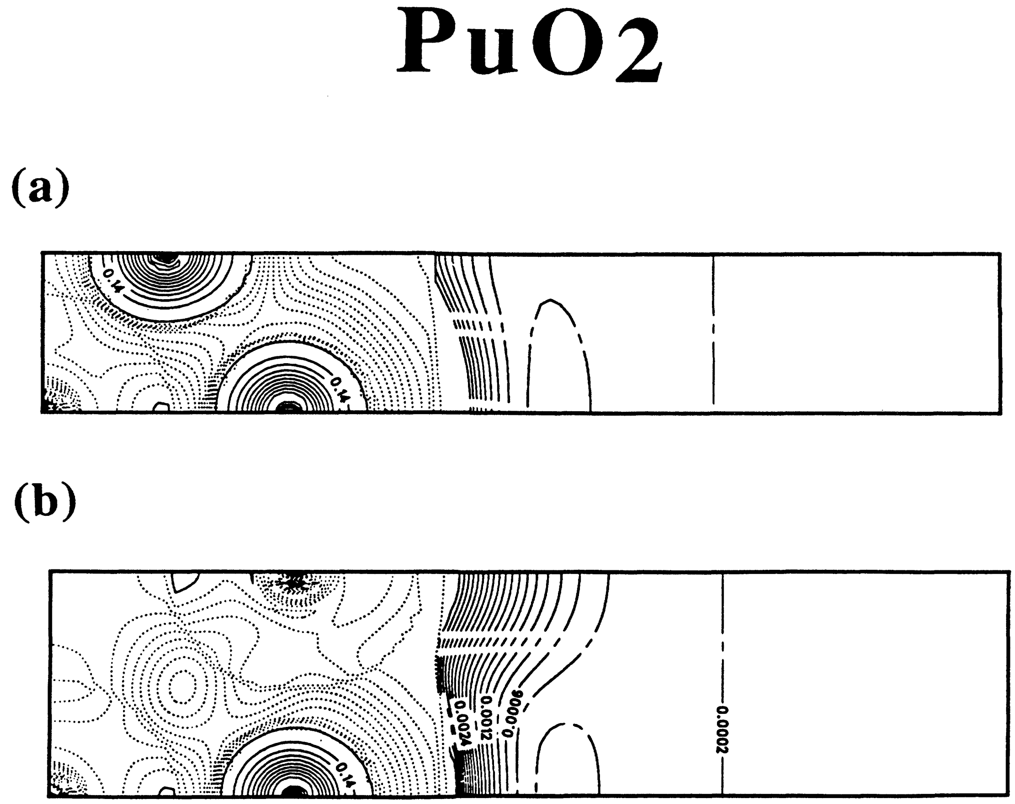

FIG. 5. Charge-density contour map (in electrons/a.u.^{3}) for PuO_2 cut along the [110] direction (a) and along the [100] direction (b). The spacing between the solid lines is 0.01, between the dotted lines 0.003, and between the dashed lines 0.0001.

standing of the induced shifts in the valence states, due to the polarized 5*f* electrons.

V. CONCLUSIONS

Often in calculations of surface electronic structure it is found that the bandwidths of the surface atoms are narrower than for the bulk atoms. This is due to the fact that the coordination number is lower at the surface. If direct overlap between nearest neighbors dominates the electronic interactions, the narrowing at the surface follows. The present investigation shows little band narrowing for the surface states and indicates that the valence electrons are highly itinerant. The surface behavior in our plutonium hydride and oxide calculations shows an interesting contrast with our results for pure metallic plutonium. There the 5*f* electrons are valence electrons and show only a small covalentlike bonding contribution associated with small 5*f* to non-5*f* band hybridization. For the hydride and oxide the Pu 5*f* electrons are well localized and are treated as core electrons, so that the plutonium valence behavior is dominated by the 6*d* electrons. This gives rise to significant hybridization with ligand valence electrons and therefore significant covalency, especially for the oxide where the important 6*d* mixing is with the valence 2*p* electrons. This shows up in the charge density, since the covalent character in the bonds piles up charge between the different atoms. Therefore, we find more charge in the interstitial region in PuH_2 (about $2e^-$/atom) and PuO_2 (about $3e^-$/atom) compared to metallic Pu (about $1e^-$/atom).

The present work also shows that the chemisorption of H and O on plutonium induces a change in the work function. This is a consequence of the chemisorbed atoms modifying the surface dipole moment. Similar effects were observed for H chemisorbed on the Ni (100) surface.[19] We also find for PuH_2 that the total energy is minimized when the H atoms are very close to the fourfold-bridging position, with only a small relaxation effect (0.01 Å out from the plane). Furthermore, we have found that there is little charge transfer between the different muffin-tin spheres, in either PuO_2 or PuH_2. Instead the hybridization between the Pu 6*d* and H 1*s* (O 2*p*) states is strong. This induces a covalent character in the bonds of both PuH_2 and PuO_2.

In our spin-polarized calculations we find that the valence electrons carry a moment of $0.22\mu_B$ per Pu atom. This reduces the total moment and accounts for the discrepancy between the measured moments from paramagnetic susceptibility measurements or neutron scattering in the ordered state and the ordered moment obtained from magnetization measurements.

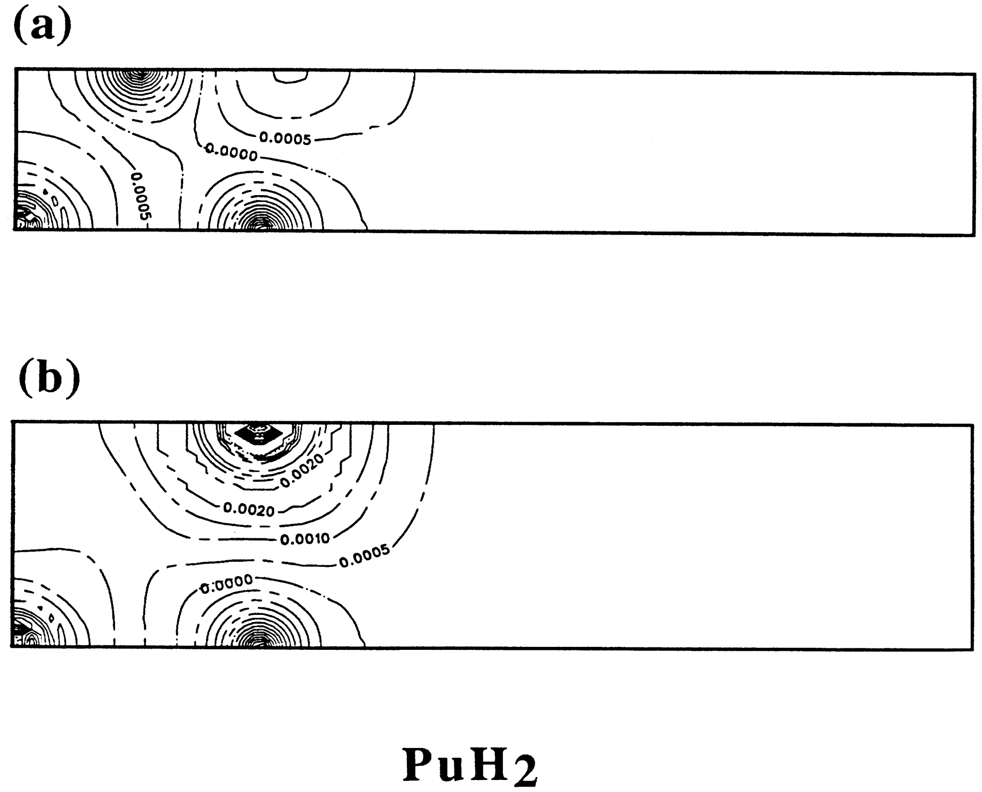

FIG. 6. Spin-density contour (in electrons/a.u.^{3}) for PuH_2 cut along the [110] direction (a) and along the [100] direction (b). The spacing between the lines is 0.005.

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