

# Molecular hydrogen adsorption and dissociation on the plutonium (111) surface

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Hydrogen molecule adsorption and the reaction barrier for dissociation on the plutonium (111) surface have been studied in detail using the generalized gradient approximation to density functional theory. All calculations have been performed at both non-spin-polarized and spin-polarized levels of the theory. Weak molecular adsorptions with a layer by layer alternate spin arrangement of the plutonium atoms were observed. Horizontal approaches on the top site both without and with spin polarization were found to be the most favorable molecular adsorption sites. For dissociative adsorption it was found that the most favorable dissociation channel needs activation energies of 0.216 and 0.305 eV at the non-spin-polarized and spin-polarized levels, respectively, with considerably higher adsorption energies than those of the molecular cases. Compared to dissociation on the (100) surface, hydrogen molecule dissociation on the (111) surface is easier because the activation energies are much lower in the later case. In general the adsorption of hydrogen molecule pushes the Pu 5*f* band away from the Fermi level, except for spin-polarized dissociative adsorption, where 5*f* orbitals come closer to the Fermi level. Charge transfer to the hydrogen atoms for dissociative adsorption is larger than that of molecular adsorption due to the reduced distances of hydrogen atoms to the plutonium surface. In that case, the ionic part of H-Pu bonding contributes along with the covalent part due to Pu 5*f*-H 1*s* hybridization.

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## I. INTRODUCTION

In recent years, advances in theoretical and computational formalisms have significantly increased research in high-*Z* strongly correlated materials and heavy fermion systems. In this area, actinides play a central role and yet, surface chemistry and physics of the actinides remain largely an unexplored territory. One of the many motivations to study the actinide surfaces is a desire to understand the signature role of the 5*f* electrons in bonding and localization as also detailed mechanisms that lead to surface corrosion in the presence of environmental gases; a problem that is not only scientifically and technologically challenging but also environmentally important. As is known, the actinides are characterized by a gradual filling of the 5*f*-electron shell as the degree of localization increases with the atomic number *Z* along the last series of the periodic table. Narrower 5*f* bands near the Fermi level, close in energy to the 7*s* and 6*d* bands, and the resulting hybridization effects are believed to be responsible for the exotic nature of actinides at ambient conditions.<sup>1</sup> Among the actinides, plutonium (Pu) is particularly interesting in two respects.<sup>2-9</sup> First, plutonium has, at least, six stable allotropes between room temperature and melting at atmospheric pressure, indicating that the valence electrons can hybridize into a number of complex bonding arrangements. Second, plutonium represents the boundary between the light actinides: Th to Pu, are characterized by itinerant 5*f* electron behavior, and the heavy actinides, Am and beyond, are characterized by localized 5*f* electron behavior.

Although the monoclinic  $\alpha$  phase of plutonium is more stable under ambient conditions, there are advantages to studying  $\delta$ -like layers. First, a very small amount of impurities can stabilize  $\delta$ -Pu at room temperature. For example, Pu<sub>1-x</sub>Ga<sub>x</sub> has the fcc structure and physical properties of  $\delta$ -Pu for 0.020 < *x* ≤ 0.085.<sup>10</sup> Second, grazing-incidence photo-

emission studies combined with the calculations of Eriksson *et al.*<sup>11</sup> suggest the existence of a small-moment  $\delta$ -like surface on  $\alpha$ -Pu. Our work on plutonium monolayers has also indicated the possibility of such a surface.<sup>12</sup> Recently, high-purity ultrathin layers of plutonium deposited on Mg were studied by x-ray photoelectron (XPS) and high-resolution valence band (UPS) spectroscopy by Gouder *et al.*<sup>13</sup> They found that the degree of delocalization of the 5*f* states depends in a very dramatic way on the layer thickness and the itinerant character of the 5*f* states is gradually lost with reduced thickness, suggesting that the thinner films are  $\delta$ -like. At intermediate thickness, three narrow peaks appear close to the Fermi level and a comparative study of bulk  $\alpha$ -Pu indicated a surface reorganization yielding more localized *f* electrons at thermodynamic equilibrium. In fact, the high temperature fcc  $\delta$  phase of plutonium exhibits properties that are intermediate between properties expected for the light and heavy actinides. Also,  $\delta$  plutonium shows negative thermal expansion coefficient and exhibits superconductivity alloyed with other elements. The unusual aspects of the bonding in bulk plutonium are apt to be enhanced at a surface or in an ultra thin film of plutonium adsorbed on a substrate, due to the reduced atomic coordination of a surface atom and the narrow bandwidth of surface states. For this reason, plutonium surfaces and films and adsorptions on these may provide a valuable source of information about the bonding in plutonium. Finally, it may be possible to study 5*f* localization in plutonium through adsorptions on carefully selected substrates for which the adsorbed layers are more likely to be  $\delta$ -like than  $\alpha$ -like.

Molecular hydrogen adsorption on metal surfaces is the simplest prototype chemical reaction to gain fundamental insight into the complex nature of any adsorbate-surface bonding. This is often the first step in many catalytic processes. Hydrogen storage problem is another issue leading to numerous studies on hydrogen and metal surface interactions. Ad-

sorption of hydrogen molecule on metals can be divided into two categories: one in which the sticking parameter increases with the incident kinetic energy of  $H_2$ , and the other where there is an initial decrease of sticking parameter with the kinetic energy. Molecular hydrogen adsorption on transition metal surfaces is often dissociative, while on noble or simple metal surfaces the adsorption might be molecular, and need some activation energies to overcome the energy barrier for dissociation.<sup>14</sup> Thus, one purpose of this work is to investigate the probability of dissociative adsorption compared to molecular adsorption of hydrogen on plutonium surface. The interactions of Pu with  $H_2$  and  $O_2$  have been investigated in several works.<sup>15</sup> In our recent study for molecular hydrogen adsorption on the Pu (100) surface, we found that hydrogen adsorption was initially molecular followed by dissociation with energy needed to overcome the reaction barrier. For the most probable dissociation channel, the activation energies were 0.551 and 0.778 eV for non-spin-polarized and spin-polarized calculations, respectively, and after dissociation, each hydrogen atom was observed to move to diagonally opposite center positions.<sup>16</sup> There are no other theoretical studies in the literature on hydrogen adsorption on the Pu surface and in fact, no detailed information exists in the literature about the magnetic state of the molecule-adsorbed surface of plutonium. We also note that as the films get thicker, the complexity of magnetic ordering, if existent, increases and such calculations are quite challenging computationally. Nevertheless, to study the effects of spin polarization on the adsorption processes, our studies for molecular hydrogen adsorption on the Pu (111) surface here, as with our studies on the Pu (100) surface, have been performed at both non-spin-polarized and at the spin-polarized levels. We first discuss the theory and computational details in brief, followed by detailed results and discussions.

## II. THEORY AND COMPUTATIONAL DETAILS

The theoretical formalism used in our computations is the generalized-gradient approximation<sup>17</sup> (GGA) to density functional theory (DFT).<sup>18</sup> This theory, in spite of its deficiencies in dealing with *some* properties of strongly correlated and heavy fermion systems, has been used by different groups to study bulk and surface properties of actinides.<sup>2-9</sup> We have reviewed the current state of the literature on DFT studies of bulk and the surface of  $\delta$ -Pu in our previous works.<sup>16</sup> Central to the issues are the atomic volume, bulk modulus, surface energies, localization, and magnetic moments, to name a few. Here we just comment on a *very few* other published works in the literature. DFT, in the local density approximation (LDA), underestimates the equilibrium volume up to 30% and predicts an approximately four times too large bulk modulus<sup>19,20</sup> compared to experimental values. The electronic structure is, in fact, incompatible with photoemission spectra. On the other hand, theories beyond LDA, such as, the self-interaction-corrected (SIC) LDA studied by Petit *et al.*<sup>21</sup> predicted a 30% too large equilibrium volume. Penicaud<sup>22</sup> performed total energy calculations in the local density approximation using fully relativistic muffin-tin orbital band structure method. For  $\delta$ -Pu, the  $5f_{5/2}$

electrons were uncoupled from the *s*, *p*, and *d* electrons to reproduce the experimental value of the equilibrium atomic volume. Also an adjustable parameter was introduced to get a better theoretical representation of  $\delta$ -Pu. As far as magnetic moment  $\delta$ -Pu is concerned, the experimental evidence remains, at this point, mostly conclusive, though controversies persist.<sup>10,23-25</sup> Susceptibility and resistivity data for  $\delta$ -Pu were published by Meot-Reymond and Fournier,<sup>23</sup> indicating the existence of small magnetic moments screened at low temperatures. This screening was attributed to the Kondo effect. Recent experiments by Curro and Morales<sup>10</sup> of 1.7% Ga-doped  $\delta$ -Pu conducted at temperatures lower than the proposed Kondo temperature of 200–300 K showed little evidence for local magnetic moments at the Pu sites. Piskunov *et al.*<sup>24</sup> studied the spin susceptibility of stabilized  $\delta$  phase in the Pu-Ga alloy by measuring <sup>69,71</sup>Ga NMR spectra and nuclear spin-lattice relaxation rate in the temperature range 5–350 K. No NMR evidences favoring formation of the static magnetic order in  $\delta$ -Pu were revealed down to 5 K. Experimental data by Lashley *et al.*<sup>25</sup> also provides no evidence for ordered and disordered magnetic moments in Pu at low temperatures. The authors, however, indicate the need for new experiments to understand the magnetic moment controversy in  $\delta$ -Pu. Though there is no direct experimental evidence for magnetic moment, spin-polarized DFT, specifically the generalized-gradient approximation (GGA) to DFT, has been used by theoreticians, in particular, to predict the magnetic ordering and the ground state properties of  $\delta$ -Pu.<sup>26-32</sup> This is partly due to the fact that spin-polarized DFT calculations do predict better agreement with photoemission data as also atomic volume and bulk modulus. Wang and Sun,<sup>27</sup> Postnikov *et al.*,<sup>28</sup> and Boettger<sup>29</sup> have shown that the antiferromagnetic state of  $\delta$ -plutonium yields better results for which physical parameters agreed well with the experiments. In a recent study Söderlind *et al.*<sup>30</sup> claimed that magnetic moments could be the defining issue for the explanation of all six phases of plutonium. Wills *et al.*<sup>31</sup> have claimed that there is, in fact, no evidence of magnetic moments in the bulk  $\delta$  phase, either ordered or disordered. Savrasov *et al.*<sup>32</sup> have studied correlated electrons in  $\delta$ -Pu within a dynamical mean-field theory (DMFT) picture. This approach, reproducing both ground- and excited-state spectra, can provide information about temperature effects and local-moment regime. To study the phase diagram of Pu, a self-consistent relativistic DMFT method was used and one of the major conclusions from this work was that the  $\alpha$  and  $\delta$  phases are on opposite sides of the interaction-driven localization-delocalization transition. This theory needs an input parameter for the effective Coulomb interaction  $U$  between *f* electrons in Pu and a value of  $U=4$  eV produces the main features of the experimental phase diagram of Pu. The theory has also been applied to calculate the phonon spectra of Pu and the predicted spectra has been found to agree well with experiments in the elastic limit.<sup>33</sup> Using the full-potential (FP) linearized-augmented-plane-wave (LAPW) method, Wu and Ray<sup>34</sup> have calculated the equilibrium atomic volume 178.3 a.u.<sup>3</sup> and bulk modulus 24.9 GPa of ferromagnetic bulk  $\delta$ -Pu at the fully relativistic level of theory, in good agreement with the experimental values of 168.2 a.u.<sup>3</sup> and 25 GPa (593 K), respectively. As expected,

within the GGA approximation to DFT, the atomic volume is slightly overestimated.

All the calculations reported in this work have been performed using the suite of programs DMOL3.<sup>35</sup> This code does not yet allow fully relativistic computations and, as such, we have used the scalar-relativistic approach. In this approach, the effect of spin-orbit coupling is omitted primarily for computational reasons, but all other relativistic kinematic effects, such as mass velocity, Darwin, and higher order terms are retained. It has been shown<sup>35</sup> that this approach models actinide bond lengths fairly well. We certainly do not expect that the inclusion of the effects of spin-orbit coupling, though desirable, will alter the primary qualitative and quantitative conclusions of this paper, particularly since we are interested in the adsorption energies defined as the difference in total energies and it is expected that the shift in total energies in Pu and Pu+H<sub>2</sub> systems due to inclusion of spin-orbit coupling is expected to basically cancel each other. Spin-orbit interaction, causing a maximum of less than a few percent volume change, may be necessary for a very accurate determination of atomic volume but is not deemed to be absolutely necessary for chemisorption studies for the reasons stated above. We also note that Landa *et al.*<sup>30</sup> and Kollar *et al.*<sup>36</sup> have observed that inclusions of spin-orbit coupling are not essential for the quantitative behavior of  $\delta$ -Pu. Hay and Martin<sup>37</sup> found that one could adequately describe the electronic and geometric properties of actinide complexes without treating spin-orbit effects explicitly. Similar conclusions have been reached by us in our study of water adsorption on PuO<sub>2</sub> (Ref. 38) and of molecular PuO<sub>2</sub> and PuN<sub>2</sub> (Ref. 39) and by Ismail *et al.*<sup>40</sup> in their study of uranyl and plutonyl ions. We also note that the scalar-relativistic hybrid density functional theory has been used by Kudin *et al.*<sup>41</sup> to describe the insulating gap of UO<sub>2</sub>, yielding a correct antiferromagnetic insulator.

In DMOL3, the physical wave function is expanded in an accurate numerical basis set, and fast convergent three-dimensional integration is used to calculate the matrix elements occurring in the Ritz variational method. A double numerical basis set with polarization functions (DNPs) has been used for the calculations. The sizes of these DNP basis set are comparable to the 6-31G\*\* basis of Hehre *et al.*<sup>42</sup> However, they are believed to be much more accurate than a Gaussian basis set of the same size.<sup>35</sup> For Pu, the outer sixteen electrons ( $6s^2 6p^6 5f^6 7s^2$ ) are treated as valence electrons and the remaining seventy-eight electrons are treated as core. A hardness conserving semilocal pseudopotential, called density functional semicore pseudopotential (DSPP), has been used. These norm-conserving pseudopotentials are generated by fitting all-electron relativistic DFT results and have a non-local contribution for each channel up to  $l=2$ , as well as a nonlocal contribution to account for higher channels. To simulate periodic boundary conditions, a vacuum layer of 30 Å was added to the unit cell of the layers. The  $k$ -point sampling  $5 \times 5 \times 1$  was done by the using the Monkhorst-Pack scheme<sup>43</sup> and the Perdew-Wang '91 functional was used for the exchange-correlation functional.<sup>17,44</sup> The maximum number of numerical integration mesh points available in DMOL3 has been chosen for our computations, and the threshold of density matrix convergence is set to

$10^{-6}$ . All computations have been performed on a Compaq ES40 alpha multiprocessor supercomputer at the University of Texas at Arlington. A more thorough treatment might require a fully relativistic Dirac treatment but such analysis is beyond the computational resources available to date.

### III. RESULTS AND DISCUSSIONS

As in our earlier studies of diatomic gas molecule adsorptions on actinide surfaces,<sup>16,45</sup> to study H<sub>2</sub> adsorption on the plutonium (111) surface, we have modeled the surface with three layers of fcc plutonium at the experimental lattice constant. No surface relaxation and reconstruction have been taken into consideration because of severe demands on computational resources and in that sense, this work should be considered as a first step towards a complete understanding of molecular hydrogen adsorption on actinide surfaces. We wish to point out, however, that the spin-polarized bulk lattice constant of  $\delta$ -Pu with our  $k$ -point sampling and the choices of pseudopotential and exchange-correlation functional is found to be 8.96 a.u. to be compared with the experimental value of 8.76 a.u.<sup>46</sup> As a comparison, the FP-LAPW value is 9.10 a.u. (Ref. 34) and the FP-LMTO value is 9.00 a.u.<sup>30</sup> Our calculated work function for the three-layer (111) surface is 3.38 eV, at the spin-polarized level of theory. Durakiewicz *et al.* recently measured the work function of polycrystalline  $\delta$ -Pu for various degrees of surface oxidation. From these measurements, the work function for clean polycrystalline  $\delta$ -Pu was estimated to be  $3.1 \pm 0.1$  eV.<sup>47</sup> Thus, the agreement between our theoretical results and available experimental data can be considered to be satisfactory. The choice of three layers is believed to be quite adequate considering the hydrogen molecule is not expected to interact with atoms beyond the first three layers. This was found to be the case in our studies of atomic oxygen and hydrogen adsorptions on the plutonium surfaces.<sup>16</sup> Recently, Ray and Boettger showed in a study of quantum size effects of  $\delta$ -plutonium surface that the surface energies converge within the first three layers for both Pu (111) and Pu (100) surfaces.<sup>48</sup> This suggested that a three-layer film should be adequate as model substrates for chemisorption studies. The unit cell for our study here contains four plutonium atoms per layer to provide an accurate representation of the molecular adsorption process. Thus, our three-layer model of the surface contains twelve plutonium atoms. For spin-polarized calculations, spin arrangements of the plutonium atoms of the bare (111) surface was optimized and the arrangements with lower total energy was used for hydrogen adsorption calculations. The H<sub>2</sub> molecule, one per unit cell, was allowed to approach the plutonium surface along three different symmetrical sites: (i) directly on top of a plutonium atom (top site), (ii) on the middle of two nearest-neighbor plutonium atoms (bridge site), and (iii) in the center of the smallest unit structures of the surfaces (center site). As the smallest unit structure of (111)  $\delta$ -like plutonium surface is an equilateral triangle, these three sites are the only symmetrically distinguishable sites. However, considering the arrangements of the second and third layer atoms, two center sites are possible, i.e., if the second layer or third layer has a

plutonium atom directly below the center of the first layer triangle. They are named the center1 and center2 sites here, respectively. In addition to this, we have also considered some positions inside the Pu three-layer slab (interstitial positions). For each of these positions, we consider several approaches for adsorption paths. They are (a) H<sub>2</sub> molecule approach is vertical to the surface (“Ver” approach), (b) H<sub>2</sub> molecule approach is parallel to the surface and parallel to the lattice vectors (“Hor1” approach), and (c) H<sub>2</sub> molecule approach is parallel to the surface and at perpendicular to the lattice vectors (“Hor2” approach). It is obvious that for both of the horizontal approaches the atoms of the hydrogen molecule H<sub>2</sub> are at the same distance from the plutonium surface, whereas for the vertical approach one hydrogen atom is closer to the surface than the other atom. For geometry optimizations, the distances of the hydrogen atoms from the surface ( $r_d$ ) and the distance between the hydrogen atoms ( $r_H$ ) were simultaneously optimized. The adsorption energies were then calculated from

$$E_c = E(\text{Pu layers}) + E(\text{H}_2) - E(\text{Pu layers} + \text{H}_2). \quad (1)$$

A positive adsorption energy thus implies the probability of adsorption. For the non-spin-polarized case, both  $E(\text{Pu layers})$  and  $E(\text{Pu layers} + \text{H}_2)$  were calculated without spin polarization, while for spin polarized adsorption energies both of these energies are spin polarized.  $E(\text{H}_2)$  is the energy of the hydrogen molecule in the ground state. The adsorption energies, and the corresponding distances are provided in Table I. The distances  $r_d$  given in the tables are the distances from the plutonium surface to the hydrogen atoms if both the hydrogen atoms are at same height or to the nearer hydrogen atom if one of them is closer to the surface than the other atom.

### A. Molecular adsorption

We first discuss the top sites without spin polarization. Figure 1 shows the optimized orientation of the hydrogen molecule on plutonium surface at all sites. Only one set of figures from the top view are shown, since in this set of calculations, the optimized non-spin-polarized and spin-polarized adsorption configurations turned out to be the same. The optimized adsorption parameters and energies are provided in Table I. For the two horizontal approaches Hor1 and Hor2 which differ by an angle of 90°, the adsorption parameters are almost the same, namely, the distances ( $r_d$ ) from the plutonium surface to the H<sub>2</sub> molecule are 2.285 and 2.289 Å, respectively, and the H-H bond lengths are stretched up to 0.798 Å each from the theoretically optimized bond length of 0.738 Å. The adsorption energy of the Hor1 approach is only 0.001 eV higher than the Hor2 approach. For the Ver approach the distance of the lower oxygen atom to the plutonium surface is 3.441 Å, with an adsorption energy of 0.097 eV. For all these three approaches the H<sub>2</sub> adsorption is molecular, the maximum increase in H-H bond length being only 0.060 Å for the Hor2 and Hor1 approaches from the theoretical bond length of H<sub>2</sub>. For both Hor1 and Hor2 approaches, the hydrogen molecule moves away from the plutonium surface if spin polarization is con-

TABLE I. Molecular hydrogen adsorption energies on the Pu(111) surface. Here,  $r_d$  and  $r_H$  are the distances of hydrogen atom from the Pu surface and the H-H distance, respectively. Magnetic moments (MMs) are listed for the spin-polarized adsorptions.

Sites	Approach	$r_d$ in Å	$r_H$ in Å	Adsorption		
				energy in eV	MM in $\mu_B/\text{atom}$	
NSP	Top	Ver	3.441	0.754	0.0968	
		Hor1	2.285	0.798	0.2999	
		Hor2	2.289	0.798	0.2989	
	Bridge	Ver	3.436	0.756	0.1116	
		Hor1	3.452	0.752	0.0699	
		Hor2	3.448	0.753	0.0979	
	Center1	Ver	2.573	0.770	0.1189	
		Hor1	2.284	0.798	0.2998	
		Hor2	2.920	0.759	0.1279	
	Center2	Ver	2.647	0.765	0.1305	
		Hor1	2.284	0.800	0.2998	
		Hor2	2.752	0.761	0.1142	
SP	Top	Ver	3.428	0.738	0.0949	1.699
		Hor1	2.372	0.762	0.1345	1.687
		Hor2	2.389	0.761	0.1367	1.687
	Bridge	Ver	3.365	0.742	0.1059	1.698
		Hor1	3.459	0.735	0.0594	1.698
		Hor2	3.448	0.736	0.0794	1.698
	Center1	Ver	3.251	0.738	0.1072	1.698
		Hor1	2.373	0.762	0.1345	1.698
		Hor2	3.131	0.741	0.1029	1.697
	Center2	Ver	2.904	0.736	0.0906	1.696
		Hor1	2.373	0.762	0.1346	1.687
		Hor2	3.187	0.739	0.1099	1.698

sidered. For example for the Hor2 approach,  $r_d$  is 0.100 Å from its non-spin-polarized counterpart. In addition to this, the H-H distances are slightly compressed compared to the non-spin-polarized cases for all approaches in the top site. For the Hor2 approach, the H-H distance after adsorption on plutonium surface is 0.761 Å, whereas the non-spin-polarized bond length, as mentioned above, is 0.798 Å. The adsorption energies are lower due to the inclusion of spin polarization, and the Hor2 approach become 0.002 eV more stable than the Hor1 approach. Unlike our earlier study of hydrogen molecule adsorption on (100) plutonium surface, the adsorption energies of hydrogen molecule on top site are sensitive on whether the hydrogen molecule is on vertical or horizontal orientations, though the two horizontal approaches of molecular adsorption remain almost degenerate in energy. This difference in (100) and (111) surface is basically due to the higher density of plutonium atoms on the (111) surface. However, for both non-spin-polarized and spin-polarized cases, Hor1 and Hor2 approaches have the highest adsorption energies at top site than the any other sites and approaches in this study.

For bridge and center sites similar situations take place, i.e., the adsorption is molecular and the H-H distances are

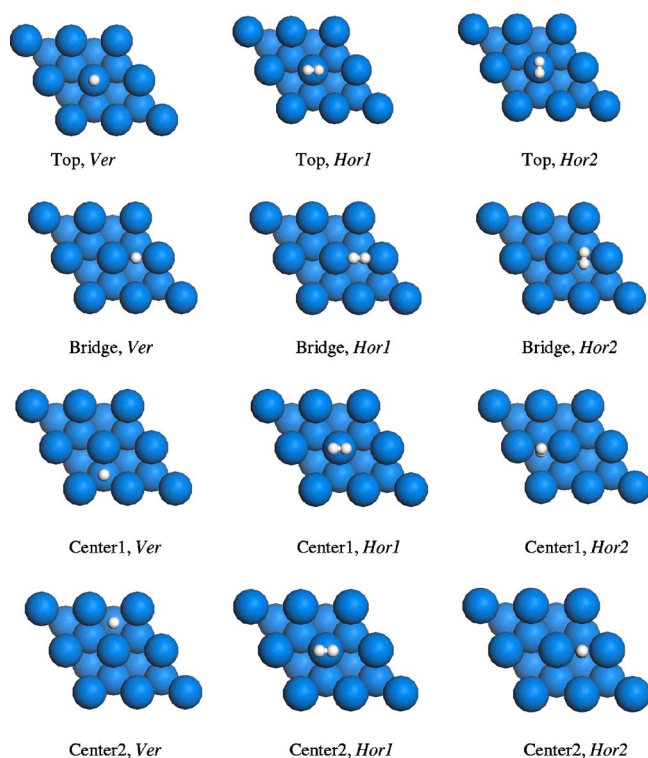


FIG. 1. (Color online) Optimized adsorption configurations for different sites and approaches. For all cases, the final orientations of the hydrogen molecule on plutonium surface are basically similar for both non-spin-polarized and spin-polarized cases.

relaxed when spin-polarization is not included and compressed due to spin polarization. For the two center sites, spin polarization has significant effect on the adsorption configuration and energies of the Ver approaches. As Ver approaches on center1 and center2 sites the adsorption energies are 0.119 and 0.131 eV without spin-polarization, respectively, while the  $r_d$ 's are 2.573 and 2.647 Å. With spin polarization these  $r_d$ 's become larger and the adsorption energies drop to 0.107 and 0.091 eV for the center1 and center2 sites, respectively. The horizontal approaches of the center sites behave almost similarly. The final optimized adsorption configurations at Hor1 approaches for both the center sites are similar to the Hor1 approach on the top site with almost the same adsorption energy. As mentioned before, this adsorption energy is the highest among the all other adsorption sites at the corresponding levels of theories.

On the other hand, the final configurations of the adsorbed hydrogen molecule at the Hor2 approach for both the center sites become nearly vertical and moved towards the bridge site (not exactly on the bridge site). For the spin-polarized optimization of this approach H<sub>2</sub> is more vertical to the plutonium surface than the non-spin-polarized case. In the non-spin-polarized case hydrogen molecule is closer to the surface, and adsorption energies are higher than the spin polarized cases. In non-spin-polarized bridge site the adsorption energy in vertical approach is 0.112 eV, whereas as Hor2 approaches the center sites they are 0.128 and 0.114 eV at center1 and center2 sites, respectively. The  $r_d$ 's for the bridge site in general are higher than the other sites men-

tioned in this study. The Hor1 and Hor2 approaches at bridge site have the lowest adsorption energies among all the horizontal approaches on different sites. For example Hor1 approach on bridge site with spin polarization has the lowest adsorption energy of 0.059 eV. Also these horizontal approaches on the bridge site in general have shorter H-H bond length after the adsorption.

From the above discussions it is clear that on the (111) plutonium surface, as on the (100) surface, adsorptions of hydrogen is mainly molecular in nature, and though all the adsorption energies are considerably small, there are noticeable variations in the adsorption energies. Also all the  $r_d$ 's are considerably large and, as a consequence, the  $r_H$ 's are similar to the optimized bond length of hydrogen molecule. In general, the variations of adsorption energies with respect to various sites and approaches can be explained with aid of the coordination number of the sites and the proximity of hydrogen atoms to plutonium atoms on the surface. First of all, the energetics of hydrogen molecule adsorptions on plutonium (111) surface differ significantly from that of the (100) surface.<sup>16</sup> As mentioned before, the main reason is that the concentration of plutonium atoms is larger on the (111) surface, so the interaction with hydrogen atom is rather complicated. We have seen in the preceding discussion that both the horizontal approaches on the top site have the highest adsorption energy. Also the Hor1 approaches of center1 and center2 sites, in their final optimized adsorption configurations, become similar to the Hor1 approach on the top site. Here hydrogen atoms for both the Hor1 and Hor2 approaches at the top site primarily interact locally with the same top-site plutonium atom with the nearest H-Pu distance of 2.319 Å (without spin polarization), yielding almost the same adsorption energies. The second nearest H-Pu distance given by the non-spin-polarized calculations are 3.484 and 3.818 Å for Hor1 and Hor2 approach, respectively, which might be accounted for the slight decrease in adsorption energy at the top site Hor2 approach. This argument does not hold for their spin-polarized counterpart. In the spin-polarized case,  $r_d$  is larger for the Hor2 approach than the Hor1 approach, and as the  $r_H$  is similar for both the approaches, consequently second nearest H-Pu distance will be larger for the Hor2 than the Hor1 approach. Still the slightly higher adsorption energy in the Hor2 approach might indicate the presence of antibonding orbital in the bonding mechanism.

We recall that for the (100) surface at the Ver approach on the center site, which is fourfold coordinated, was the energetically favorable molecular adsorption configurations.<sup>45</sup> The Ver approaches on the center sites here for the (111) surface is threefold coordinated and has in general slightly higher adsorption energy (except for the spin-polarized Ver approach on the center 2 site) than the Ver approach on the bridge site, and top site, which are twofold and onefold coordinated, respectively. So, this pattern of the adsorption energies favors the sites with higher coordination. It is interesting to observe the final optimized adsorption configurations for the Hor2 approaches of both the center sites. In the input configurations at Hor2 approach on center site the hydrogen molecule is basically along the median of the triangle, so one of the hydrogen atom in H<sub>2</sub> molecule interacts with one plu-

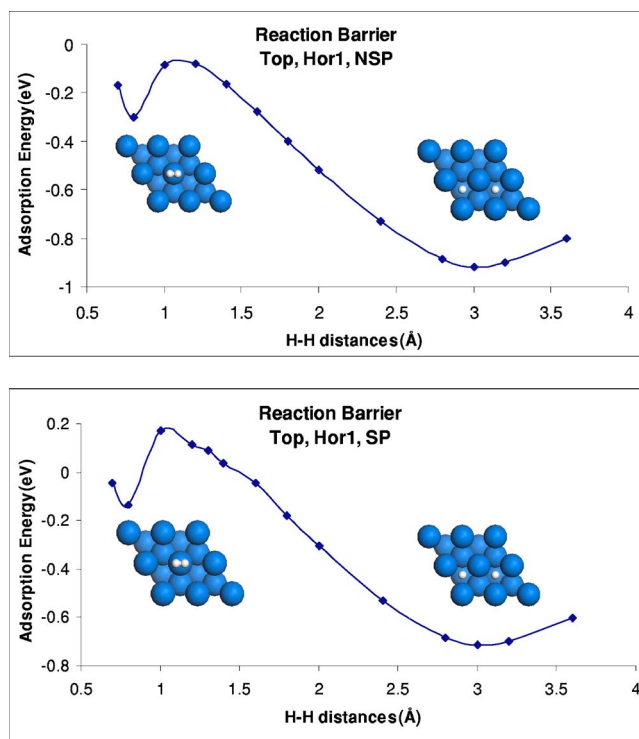


FIG. 2. (Color online) Reaction barrier for the Hor1 approach at the top site for both non-spin-polarized (NSP) and spin-polarized (SP) levels.

onium atom, and the other one interacts with the two plutonium atoms situated on the base of the triangle. The latter interaction is obviously stronger than the previous one. So, these two plutonium atoms pull the hydrogen atom on their side towards them, and as a result the whole hydrogen molecule comes almost to the middle of those two plutonium atoms, the site which is defined as the bridge site.

Different interstitial positions in the above symmetrical sites were also studied, and all the sites and approaches yielded negative adsorption energies, where the adsorption energies were calculated with respect to the molecular hydrogen energy. This means that the hydrogen molecule cannot be adsorbed for those sites inside the three plutonium layers. Though, similar to the (100) surface interstitial study for the Ver approach at the center1 site one hydrogen atom goes above the surface, and the other one stays below the top layer, the adsorption energy remained negative. From this we can infer that, at the initial stage of hydrogen adsorption on plutonium surfaces, hydrogen molecule form a weakly bonded layer above the surface. However, diffusion into the bulk to form plutonium hydride may need the dissociation of hydrogen molecule for which some activation energy might be needed. This feature is discussed in the following section.

### B. Dissociative adsorption

To study the dissociation processes of the hydrogen molecule on the plutonium (111) surface, we studied reaction barrier by constraint minimization of energy along a chosen reaction coordinate. For the sake of brevity, only the most

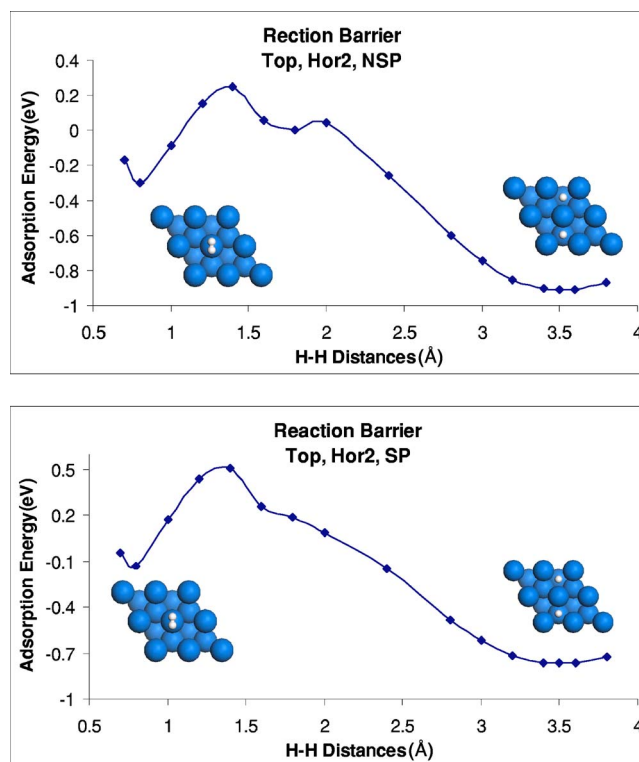


FIG. 3. (Color online) Reaction barrier for the Hor2 approach at top site for both non-spin-polarized and spin-polarized levels.

favorable molecular adsorption sites at both the non-spin-polarized and the spin-polarized levels will be considered, the reason being that the probabilities of hydrogen molecule adsorption at these sites are higher, and the molecular adsorptions might be followed by dissociation provided enough energy is supplied to overcome the dissociation barrier. Thus, both the Hor1 and the Hor2 approaches on the top site at both spin-polarized and non-spin-polarized levels will be treated as the initial dissociation channel. As for the reaction coordinate, we have chosen the H-H distances, starting at a bond length slightly below the experimental bond length. For reaction barrier calculations, at each step  $H_2$  was placed above the plutonium surface with the H-H distance kept fixed at a given value, and geometry optimization was performed to yield the total energy of the system. Figures 2 and 3 show the optimized adsorption energy curves with respect to several H-H distances. The energies are plotted with an extra negative sign to have a minima at higher adsorption energy point. We first consider the Hor1 approach of the top site. In Fig. 2 the first minimum of the curve shows the molecular adsorption near the optimized  $H_2$  bond length, similar to the situation as described before at this orientation in Sec. III A where molecular adsorption is discussed. The second minimum occur at an H-H distance of 3.00 Å, where each hydrogen atom sits nearly on two adjacent center2 sites across a bridge site, with an adsorption energy of 0.918 eV without spin polarization, while inclusion of spin polarization gives somewhat lower adsorption energy, namely, 0.713 eV. However, the curve has a maximum at a H-H distance of 1.00 Å. Between the two minima of the curve, there exists an energy hill of 0.216 eV without spin polariza-

TABLE II. Charge and spin distributions of bare plutonium layers and the most favorable adsorption configurations for non-spin-polarized and spin-polarized cases before (NSP Hor1 at top site and SP Hor2 at top site) and after dissociation (NSP and SP, Hor1 at top site) of H<sub>2</sub>.

	Plutonium layers			Plutonium+Hydrogen layers					
	NSP		SP	Molecular			Dissociative		
	Charge	Charge	Spin	Charge	Charge	Spin	Charge	Charge	Spin
H atom				-0.010	-0.007	0.016	-0.107	-0.159	-0.054
				-0.010	-0.007	0.016	-0.107	-0.159	-0.054
layer1	-0.118	-0.111	5.528	-0.095	-0.110	5.479	-0.041	-0.019	5.398
	-0.118	-0.111	5.528	-0.115	-0.098	5.500	-0.027	0.020	5.298
	-0.118	-0.111	5.528	-0.086	-0.051	5.414	-0.039	0.010	5.289
	-0.118	-0.111	5.528	-0.095	-0.110	5.479	-0.041	-0.019	5.398
layer2	0.236	0.221	-5.111	0.222	0.209	-5.104	0.200	0.181	-5.114
	0.236	0.222	-5.111	0.222	0.210	-5.099	0.239	0.226	-5.103
	0.235	0.221	-5.111	0.227	0.211	-5.113	0.239	0.226	-5.103
	0.236	0.221	-5.111	0.222	0.209	-5.104	0.200	0.181	-5.114
layer3	-0.118	-0.111	5.528	-0.119	-0.113	5.532	-0.126	-0.118	5.530
	-0.118	-0.111	5.528	-0.120	-0.114	5.531	-0.131	-0.125	5.535
	-0.118	-0.111	5.528	-0.123	-0.116	5.536	-0.132	-0.126	5.536
	-0.118	-0.111	5.528	-0.119	-0.114	5.532	-0.126	-0.118	5.530

tion and 0.305 eV with spin polarization. These energies are defined as the activation energies to be supplied at 0 K to proceed to the dissociation process. Figure 3 shows the reaction barrier curve for Hor2 approach on the top sites. Here again, the first minimum of the curve represents the molecular adsorption cases as described above, while the second minimum shows the complete dissociation of hydrogen molecule on plutonium surface. In this case the H-H distance is larger than the previous case, namely, 3.50 Å with an adsorption energy of 0.913 eV. Here after dissociation one of the hydrogen atoms sits almost on the center1 site and the other on center2 site across the top site plutonium atom, at a distance of 1.373 and 1.357 Å from the surface, without spin polarization. The energy barrier in this dissociation path is 0.545 eV. With spin polarization the adsorption configuration remains almost the same with an adsorption energy at an H-H distance of 3.50 Å of 0.769 eV and where the energy barrier for the dissociation of the hydrogen molecule is 0.644 eV. As can be seen from this discussion, the Hor1 approach has slightly higher adsorption energy at the non-spin-polarized level at the dissociation minimum, than at the corresponding minimum for the Hor2 approach. As in the molecular adsorption case, here the spin-polarized case also gives an opposite picture. However, the activation energies are much less in Hor1 approach than those of the Hor2 approach. So we can conclude that the Hor1 approach on top site, where after dissociation each of the hydrogen atom sits on the center2 sites is the preferable channel for the reaction pathway for hydrogen dissociation on the plutonium (111) surface. From our atomic hydrogen adsorption study on the plutonium surface on the (111) surface<sup>16</sup> we know that the preferable site for the atomic hydrogen adsorption is on the site we define here as the center2 site. Also here we note that

for the molecular hydrogen adsorption on the (100) plutonium surface,<sup>16</sup> we found that the dissociation path where each hydrogen atom goes to the center sites across the top atom was the most favorable dissociation channel with, however, lower adsorption energies compared to that of the (111) surface. The higher adsorption energies for the (111) surface than that of the (100) surface is also consistent with our earlier atomic adsorption study. From the trend of reaction barrier for hydrogen molecule dissociation paths, as discussed here, we can see that inclusion of spin polarization usually raises the barrier, and the extra energy that is needed to break up the H<sub>2</sub> is clearly to overcome the magnetic part of the potential. In either of the horizontal approaches, after dissociation, the adsorption is basically atomic in nature.

### C. Discussions

Table II lists the Mulliken charge distributions<sup>49</sup> for the bare plutonium layers and the most favorable hydrogen adsorbed sites, namely, the Hor1 approaches of the top sites for non-spin-polarized molecular and both non-spin-polarized and spin-polarized dissociative adsorptions and the spin-polarized molecular adsorption at Hor2 approach. The particular symmetry of the charge distribution for the bare plutonium layers, as can be seen from Table II, reflects the symmetry of the unit cell chosen for the calculations. The overall charge distribution patterns for both adsorption sites are almost same. In general, it is found that upon adsorption on plutonium surface, hydrogen molecule acquires slightly negative charges from the plutonium layers. For instance, in the case for molecular adsorption, after the adsorption of hydrogen molecule on top site both the hydrogen atoms acquire very small negative charges, for instance,  $-0.010e$  for

the non-spin-polarized case with the Hor1 approach and  $-0.007e$  for the spin-polarized case with the Hor2 approach. The top site plutonium atom, which is directly below the hydrogen molecule, loses more charges to the hydrogen molecule compared to the plutonium atoms around it, which is expected. However, since the surrounding plutonium atoms also lose charges when compared with the bare plutonium top layers, we conclude that at the top site the hydrogen molecule not only interacts with the plutonium atom directly below it, but also with the surrounding plutonium atoms, though the interaction is weaker. Basically, as the hydrogen molecule and the plutonium top layer both are slightly negatively charged, the Coulomb interaction is repulsive. However, in the equilibrium molecular adsorption configuration, as listed in Tables I and II, the total charge transfer to  $H_2$  from the plutonium slab is not significant, and hence the contribution of ionic part in the Pu-H bonding is not significant. Also, as expected, for molecular hydrogen adsorption on plutonium layers, the second and third layer charge distributions are almost the same compared to the corresponding bare cases. In the case of dissociative adsorption, there is considerable amount of the charge transfer from the plutonium surface to hydrogen atoms compared to the molecular adsorption. For non-spin-polarized calculation, each hydrogen atom gets a  $-0.107e$  charge mainly from the top plutonium layer, and as a consequence the top layer plutonium atoms become less negative than the bare plutonium layers. For the spin-polarized case the charge transfer is more significant, with  $-0.159e$  per hydrogen atom and as a consequence some of the top layer plutonium atoms become slightly positive. The plutonium atoms in the third layer directly below the hydrogen atoms are less negative than the surrounding plutonium atoms. For dissociative adsorption, the charge distributions in the second and third layers are slightly modified. For the spin-polarized case, the spin arrangements on the surface affect the charge distribution, though the overall pattern remains the same. However, from the fact that the second and third layers of both non-spin-polarized and spin-polarized hydrogen adsorbed plutonium surfaces remain almost the same as the bare plutonium layers, we can infer that the effects of hydrogen adsorptions decay significantly beyond the third layer.

The magnetic moments of the hydrogen adsorbed plutonium layers for different adsorption configurations are tabulated in Table I, and in Table II the distribution of spin-magnetic moments are shown. Though, as mentioned in the Introduction, no local magnetic moment has been found experimentally for bulk  $\delta$  plutonium, due to the reduced dimensionality and narrow surface states plutonium thin layers and surfaces might show some magnetic moments. In this study, the average magnetic moment of bare plutonium layers is found to be  $1.982\mu_B$  per atom with layer by layer alternating spin arrangement. Table II has the distribution of spins for bare plutonium layers, which shows basically an antiferromagnetic-type behavior, in agreement with some theoretical calculations for bulk Pu.<sup>27-29</sup> The first and third layers have up spins of the same magnitude, while the second layer has down spins with slightly lower spin moments. As with (100) surface,<sup>16,45</sup> for the (111) surface other spin arrangements also yield higher total energies than the anti-

ferromagnetic one. The average magnitude of the local spin magnetic moment for each of the plutonium atom in the slab is about  $5.398\mu_B$ , which indicate a large part of  $5f$  electrons could be localized. The same comment is equally valid for the hydrogen adsorbed plutonium layers.

The changes in the spin-magnetic moment of the hydrogen-plutonium system due to the adsorption of hydrogen molecule are slightly lower, giving an average value of  $1.687\mu_B$  per atom for the most preferred adsorption site. All of the average magnetic moments, as shown in Table I for molecular adsorption, have about the same magnitude. The moment on the adsorbed hydrogen molecule is negligible. Table II also shows the spin distribution of the top site of the Hor1 approach for molecular and dissociative adsorptions, which again shows an almost layer by layer alternate spin arrangement similar to the bare plutonium surface, which might be a precursor of antiferromagnetic behavior. The same is true for all the other sites of spin polarized cases. In the molecular adsorption case, the spin distributions on the plutonium atoms are almost the same as the bare case, whereas for dissociative adsorption the distribution is slightly different. For dissociative adsorption, the average magnetic moment per atom  $1.641\mu_B$  is further lowered from the molecular hydrogen adsorption. However, in this case moments of the two dissociated hydrogen atoms are slightly higher than those for molecular adsorptions,  $0.054\mu_B$  per atom. As discussed in this paper, the inclusion of spin polarization does not significantly change the qualitative description of the hydrogen molecule adsorption process above the surface.

As mentioned in the magnetic moment discussion above that the majority of plutonium  $5f$  electrons in the three layers of (111) surface are localized, as in our study of (100) surface, while only a fraction of  $5f$  electrons appear to be delocalized. This comment also applies to the non-spin-polarized (111) surface, though the degree of localization should be less. However, inclusion of spin polarization modified the band energetics of the bare and hydrogen adsorbed plutonium layers, though the spin up and spin down band splitting is small, i.e., itinerant magnetism is not significant here. Magnetism here is due to the localization of electrons to the particular atomic site. So inclusion of spin polarization does localize more electrons than its non-spin-polarized counterpart. The affect of spin polarization on band energy can easily be seen from the shift of the  $5f$  band. For example, the energy differences for the top of  $5f$  bands of the plutonium (111) surface and the Fermi energy  $\Delta E_{5f}$  without spin polarization is 0.287 eV, as compared with the spin-polarized value of 0.508 eV. Also, the occupation number for the top energy level of the  $5f$  band is 0.842 and 0.935 without and with spin polarization, respectively. This shows the higher localization of  $5f$  electrons when spin polarization is included. For the hydrogen adsorbed layers, for the sake of brevity, we will discuss only the most favorable molecular and dissociative adsorption configurations here. As mentioned before, for molecular adsorption these are the Hor1 approach of the top site for the non-spin-polarized and the Hor2 approach for the spin-polarized cases; and for the dissociative adsorption both at the Hor1 approach on the top site. For the molecular adsorption sites the energy differences



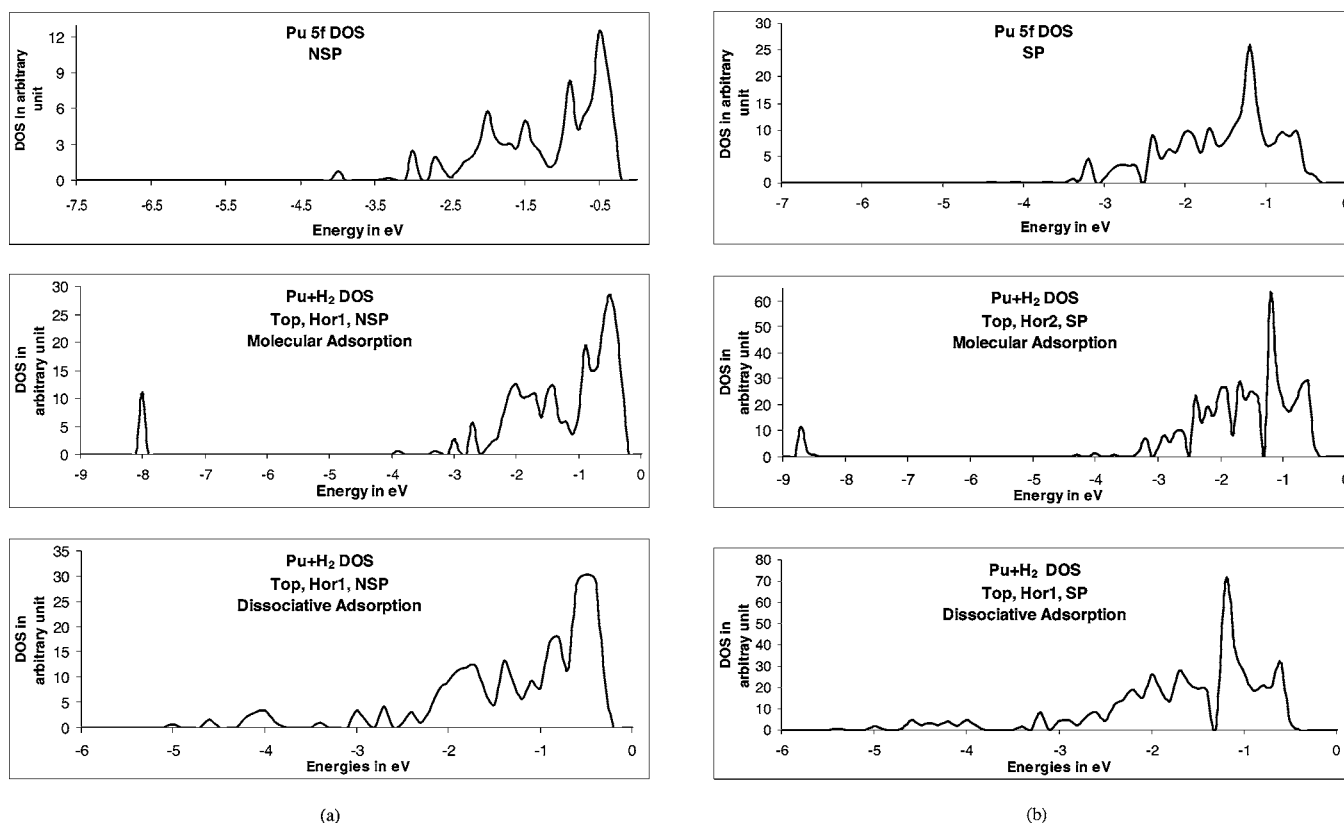


FIG. 4. Pu  $5f$  and  $H_2$   $1s$  DOS plots for the both molecular and dissociative adsorption of  $H_2$  at (a) non-spin-polarized and (b) spin-polarized levels. The Fermi energy is scaled to 0.0 eV. The first plot in each case is the bare Pu  $5f$  DOS.

for the top of the  $5f$  bands and the Fermi energy  $\Delta E_{5f}$  are 0.303 and 0.512 eV without and with spin polarization, respectively. So the non-spin-polarized case,  $\Delta E_{5f}$  is significantly different from that of the bare plutonium layer, whereas for the spin-polarized case  $\Delta E_{5f}$  remains about the same as the bare layers. The reason might be that in the spin-polarized case the hydrogen molecule is at a higher distance compared to its non-spin-polarized case. On the other hand, for dissociative adsorption the  $\Delta E_{5f}$ 's are 0.304 and 0.469 eV for non-spin-polarized and spin-polarized cases, respectively. It is interesting to see here that for the non-spin-polarized case  $\Delta E_{5f}$  remains almost the same as the molecular hydrogen adsorbed layer, whereas for the spin-polarized case  $\Delta E_{5f}$  is reduced even compared to the bare plutonium surface. This is consistent with our atomic hydrogen adsorption calculations<sup>16</sup> where we also found a reduction in  $\Delta E_{5f}$  for the hydrogen atom adsorbed spin-polarized (111) surface. The reason for the decrement in  $\Delta E_{5f}$  is that in the spin-polarized case as the electrons are becoming more localized, they tend to fill the antibonding orbitals. This in turn raises the top of the  $5f$  band near the Fermi level. Also occupation in the antibonding orbitals explains the lower adsorption energies in the spin-polarized case in Table I.

In Figs. 4(a) and 4(b) we have plotted  $5f$ -DOS for plutonium (111) bare surfaces and the most favorable hydrogen adsorbed surfaces at both non-spin-polarized and spin-polarized levels, respectively. A Gaussian broadening procedure has been employed here to compute the DOS.<sup>38</sup> A Gaussian  $\exp(-ax^2)$  is assigned to each energy eigenvalue

with  $\alpha=1000$ , such that the width at the half height is 0.05 eV. In all the DOS plots the Fermi levels are scaled to zero. From the molecular hydrogen adsorption DOS it is clear that there is no hybridization between the plutonium  $5f$  orbitals and the hydrogen  $1s$  orbitals. From both the hydrogen molecule adsorbed non-spin-polarized and spin-polarized DOS plots, we see that the energy gap between the plutonium  $5f$  and hydrogen  $1s$  orbitals is rather large, namely, around 5.000 eV. Hence, the bonding between the hydrogen molecule and the plutonium surface is very weak, possibly Van der Waals type. However, the overall pattern of the DOS is affected by hydrogen adsorption. From the spin-polarized DOS it can be seen that, there is nearly a splitting in  $5f$  band at 1.3 eV below the Fermi level due to the introduction of hydrogen, for both molecular and dissociative adsorptions. For non-spin-polarized DOS such splitting is not found near the Fermi level. However, there is another significant difference between the non-spin-polarized and spin-polarized DOS plots. The major peak of the DOS curve for the non-spin-polarized case is near the top edge of the  $5f$  band, whereas for the spin-polarized case the major peak occurred near at 1.200 eV below the Fermi level. This shows that the probability of the majority of the  $5f$  electrons being located much below the Fermi level for the spin-polarized case is higher, compared to the situation where spin polarization is not considered. In non-spin-polarized case the majority of the  $5f$  electrons tend to stay near the Fermi level. If we compare the spin-polarized bare plutonium and hydrogen adsorbed plutonium DOS, shown in Fig. 4(b), we see that

another smaller peak near the top edge of the  $5f$  level become sharper as the hydrogen adsorbed for both the molecular and dissociative adsorptions. This implies that the hydrogen adsorption localizes some of the  $5f$  electrons near the Fermi level. These two peaks are sharper in the molecular adsorption case than that of the dissociative adsorption. In Fig. 4(a), for non-spin-polarized bare plutonium  $5f$ -DOS there is a second peak at 0.8 eV below the Fermi level which become less prominent as hydrogen is adsorbed, and as consequence the major peak near the Fermi level become broader compared to the bare plutonium layers. We also see from the corresponding DOS plot of Figs. 4(a) and 4(b) that for dissociative adsorption there exists some hybridization of Pu  $5f$  and  $H_2$   $1s$  orbitals, and so the bonding between the dissociated hydrogen atoms and plutonium surface is basically a mixed ionic-covalent bonding.

The change in Fermi energy due to the adsorption of molecular hydrogen is 0.023 eV and  $-0.053$  eV without and with spin polarization, respectively, for the corresponding most favorable adsorption sites. Thus for the spin-polarized case work function is decreasing. For the dissociated hydrogen adsorption these values are 0.355 and 0.353 eV, respectively. In our previous study of hydrogen atom adsorptions on plutonium (111) surface, the work functions increment were slightly less but comparable, namely, 0.313 and 0.337 eV at non-spin-polarized and spin-polarized levels, respectively. In general, the work function increases due to dissociative adsorption of the hydrogen molecule. For molecular adsorption it remains almost the same. This holds true for all the hydrogen adsorbed sites above the surfaces.

#### IV. CONCLUSIONS

Hydrogen molecule adsorption and its dissociation on a plutonium (111) surface have been studied using the generalized gradient approximation to density functional theory. As in the (100) surface, weak molecular adsorptions with a layer by layer alternate spin arrangement of the plutonium atoms were observed. The average spin magnetic moment for bare and hydrogen adsorbed plutonium layers are  $1.982\mu_B$  and  $1.698\mu_B$  respectively, with the magnitude of individual plutonium atom spin-magnetic moment of more

than  $5.000\mu_B$ , which indicate a more localized  $5f$  electronic picture. Horizontal approaches on the top site both without and with spin polarization were found to be the most favorable molecular adsorption site, with corresponding adsorption energies of 0.299 eV (Hor1 approach) and 0.137 eV (Hor2 approach), respectively. We also studied dissociative adsorptions along with the reaction barrier for the dissociation. It was found that the most favorable dissociation channel needs activation energies of 0.216 and 0.305 eV at non-spin-polarized and spin-polarized levels, respectively, with considerably higher adsorption energies than the molecular cases, namely, 0.918 and 0.713 eV. Compared to dissociation on the (100) surface, hydrogen molecule dissociation on the (111) surface is easier because the activation energies are much lower in the later case. In general, adsorption energies of non-spin-polarized calculations are higher than the spin-polarized one, though the adsorption orientations are almost similar in both the cases. This can be attributed to filling of the antibonding orbitals as spin polarization is included. We also found that the  $5f$  electrons are more localized in spin polarized case, than their non-spin-polarized counterparts. In general, adsorption of the hydrogen molecule pushes the Pu  $5f$  band away from the Fermi level, except for the spin-polarized dissociative adsorption, where  $5f$  orbitals comes slightly closer to the Fermi level. However, the partial DOS for the plutonium  $5f$  electrons shows that for the spin-polarized adsorptions, the majority of  $5f$  electrons concentrate about 1.2 eV below the Fermi level, while for the non-spin-polarized case the peaks occur near the Fermi level. Charge transfer to the hydrogen atoms for the dissociative adsorption is larger than that of the molecular adsorption due to reduced distances of hydrogen atoms to the plutonium surface. The ionic part of H-Pu bonding plays a significant role in the dissociative adsorption, along with the covalent part due to Pu  $5f$ -H  $1s$  hybridization.

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<sup>1</sup>P. Söderlind, O. Eriksson, B. Johansson, J. M. Wills, and A. M. Boring, *Nature* (London) **374**, 524 (1995).

<sup>2</sup>J. J. Katz, G. T. Seaborg, and L. R. Morss, *The Chemistry of the Actinide Elements* (Chapman and Hall, London, 1986).

<sup>3</sup>*Transuranium Elements: A Half Century*, edited by L. R. Morss and J. Fuger (American Chemical Society, Washington, D.C., 1992).

<sup>4</sup>L. R. Morss, in *Actinides—Basic Science, Applications and Technology*, edited by L. Soderholm *et al.*, Mater. Res. Soc. Symp. Proc. No. 802 (Materials Research Society, Warrendale, PA, 2004), p. DD4.1.1.

<sup>5</sup>*Plutonium Futures—The Science*, edited by K. K. S. Pillay and K. C. Kim, Ann. Isr. Phys. Soc. No. 532 (AIP, Melville, 2000).

<sup>6</sup>*Plutonium Futures—The Science*, edited by G. D. Jarvinen, Ann. Isr. Phys. Soc. No. 673 (AIP, Melville, 2003).

<sup>7</sup>A. M. Boring and J. L. Smith, *Los Alamos Sci.* **1**, 90 (2000).

<sup>8</sup>*Advances in Plutonium Chemistry 1967–2000*, edited by D. Hoffman (American Nuclear Society, La Grange, Illinois and University Research Alliance, Amarillo, Texas, 2002).

<sup>9</sup>*Actinides—Basic Science, Applications and Technology* (Ref. 4).

<sup>10</sup>N. J. Curro and L. Morales, in *Actinides—Basic Science, Applications and Technology* (Ref. 4), p. 53.

<sup>11</sup>O. Eriksson, Y.-G. Hao, B. R. Cooper, G. W. Fernando, L. E.

- Cox, J. W. Ward, and A. M. Boring, *Phys. Rev. B* **43**, 4590 (1991); Y.-G. Hao, O. Eriksson, G. W. Fernando, and B. R. Cooper, *ibid.* **43**, 9467 (1991); B. R. Cooper, O. Eriksson, Y.-G. Hao, and G. W. Fernando, in *Transuranium elements: A Half Century* (Ref. 3), p. 365.
- <sup>12</sup>A. K. Ray and J. C. Boettger, *Eur. Phys. J. B* **27**, 429 (2002).
- <sup>13</sup>T. Gouder, *J. Alloys Compd.* **271-273**, 841 (1998); *J. Electron Spectrosc. Relat. Phenom.* **101-103**, 419 (1999); T. Gouder, L. Havela, F. Wastin, and J. Rebizant, *Europhys. Lett.* **55**, 705 (2001).
- <sup>14</sup>G. Lee and E. W. Plummer, *Phys. Rev. B* **51**, 7250 (1995).
- <sup>15</sup>J. M. Haschke, A. E. Hodges III, and R. L. Lucas, *J. Less-Common Met.* **133**, 155 (1987); J. M. Haschke, in *Synthesis of Lanthanide and Actinide Compounds*, edited by G. Meyer and L. R. Morss (Kluwer Academic Publishers, Dordrecht, 1991); J. W. Ward and J. M. Haschke, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneider, Jr., L. Eyring, G. Choppin, and G. H. Lander (Elsevier Science Publishing, Amsterdam, 1994), Vol. 18; J. L. Stakebake, *J. Alloys Compd.* **187**, 271 (1992); J. M. Haschke, T. H. Allen, and J. L. Stakebake, *ibid.* **243**, 23 (1996); J. M. Haschke, T. H. Allen, and L. A. Morales, *ibid.* **314**, 78 (2001).
- <sup>16</sup>M. N. Huda and A. K. Ray, *Physica B* **352**, 5 (2004); *Eur. Phys. J. B* **40**, 337 (2004); **43**, 131 (2005); M. N. Huda, Ph.D. thesis, The University of Texas at Arlington, 2004.
- <sup>17</sup>J. P. Perdew, in *Electronic Structure of Solids*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991); J. P. Perdew, K. Burke, and Y. Wang, *Phys. Rev. B* **54**, 16533 (1996); J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>18</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965); *Density Functional Theory for Many Fermion Systems*, edited by S. B. Trickey (Academic, San Diego, 1990); R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to Quantum Many Body Problem* (Springer, Berlin, 1990); *Electronic Density Functional Theory—Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998).
- <sup>19</sup>V. P. Antropov, M. Schilfgaard, and B. N. Harmon, *J. Magn. Magn. Mater.* **144**, 1355 (1995).
- <sup>20</sup>L. Vitos, J. Kollar, and H. L. Skriver, *Phys. Rev. B* **55**, 4947 (1997); J. Kollar, L. Vitos, and H. L. Skriver, *ibid.* **55**, 15 353 (1997).
- <sup>21</sup>L. Petit, A. Svane, W. M. Temmerman, and Z. Szotek, *Solid State Commun.* **116**, 379 (2000).
- <sup>22</sup>M. Penicaud, *J. Phys.: Condens. Matter* **9**, 6341 (1997); **12**, 5819 (2000).
- <sup>23</sup>S. Meot-Reymond and J. M. Fournier, *J. Alloys Compd.* **232**, 119 (1996).
- <sup>24</sup>Y. Piskunov, K. Mikhalev, A. Gerashenko, A. Pogudin, V. Ogloblichev, S. Verkhovskii, A. Tankeyev, V. Arkhipov, Y. Zouev, and S. Lekomstev, *Phys. Rev. B* **71**, 174410 (2005).
- <sup>25</sup>J. C. Lashley, A. C. Lawson, R. J. McQueeney, and G. H. Lander, cond-mat/0410634 (unpublished).
- <sup>26</sup>A. M. N. Niklasson, J. M. Wills, M. I. Katsnelson, I. A. Abrikosov, O. Eriksson, and B. Johansson, *Phys. Rev. B* **67**, 235105 (2003).
- <sup>27</sup>Y. Wang and Y. Sun, *J. Phys.: Condens. Matter* **12**, L311 (2000).
- <sup>28</sup>A. V. Postnikov and V. P. Antropov, *Comput. Mater. Sci.* **17**, 438 (2000).
- <sup>29</sup>J. C. Boettger, *Int. J. Quantum Chem.* **95**, 380 (2003).
- <sup>30</sup>P. Söderlind, *Europhys. Lett.* **55**, 525 (2001); P. Söderlind, A. L. Landa, and B. Sadigh, *Phys. Rev. B* **66**, 205109 (2002); P. Söderlind and A. Landa, *Modell. Simul. Mater. Sci. Eng.* **11**, 851 (2003); A. Landa, P. Söderlind, and A. Ruban, *J. Phys.: Condens. Matter* **15**, L371 (2003); P. Söderlind, J. M. Wills, B. Johansson, and O. Eriksson, *ibid.* **55**, 1997 (1997); P. Söderlind and B. Sadigh, *Phys. Rev. Lett.* **92**, 185702 (2004).
- <sup>31</sup>J. M. Wills, O. Eriksson, A. Delin, P. H. Andersson, J. J. Joyce, T. Durakiewicz, M. T. Butterfield, A. J. Arko, D. P. Moore, and L. A. Morales, *J. Electron Spectrosc. Relat. Phenom.* **135**, 163 (2004).
- <sup>32</sup>S. Y. Savrasov, G. Kotliar, and E. Abrahams, *Nature (London)* **410**, 793 (2001); G. Kotliar and D. Vollhardt, *Phys. Today* **57**, 53 (2004).
- <sup>33</sup>X. Dai, S. Y. Savrasov, G. Kotliar, A. Migliori, H. Ledbetter, and E. Abrahams, *Science* **300**, 953 (2003); J. Wong, M. Krisch, D. L. Farber, F. Occelli, A. J. Schwartz, T.-C. Chiang, M. Wall, C. Boro, and R. Xu, *ibid.* **301**, 1078 (2003).
- <sup>34</sup>X. Wu and A. K. Ray (unpublished).
- <sup>35</sup>B. Delley, *J. Chem. Phys.* **92**, 508 (1990); *Int. J. Quantum Chem.* **69**, 423 (1998); *J. Chem. Phys.* **113**, 7756 (2000); A. Kessi and B. Delley, *Int. J. Quantum Chem.* **68**, 135 (1998).
- <sup>36</sup>L. Vitos, J. Kollar, and H. L. Skriver, *Phys. Rev. B* **55**, 4947 (1997); J. Kollar, L. Vitos, and H. L. Skriver, *ibid.* **55**, 15 353 (1997).
- <sup>37</sup>P. J. Hay and R. L. Martin, *J. Chem. Phys.* **109**, 3875 (1998).
- <sup>38</sup>X. Wu, Ph.D. thesis, The University of Texas at Arlington, 2001; X. Wu and A. K. Ray, *Phys. Rev. B* **65**, 085403 (2002); *Physica B* **293**, 362 (2001); **301**, 359 (2001); *Eur. Phys. J. B* **19**, 345 (2001).
- <sup>39</sup>E. F. Archibong and A. K. Ray, *J. Mol. Struct.: THEOCHEM* **530**, 165 (2000).
- <sup>40</sup>N. Ismail, J.-L. Heully, T. Saue, J.-P. Daudey, and C. J. Marsden, *Chem. Phys. Lett.* **300**, 296 (1999).
- <sup>41</sup>K. N. Kudin, G. E. Scuseria, and R. L. Martin, *Phys. Rev. Lett.* **89**, 266402 (2002).
- <sup>42</sup>W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
- <sup>43</sup>H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- <sup>44</sup>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992); **48**, 4978 (1993).
- <sup>45</sup>M. N. Huda and A. K. Ray, *Int. J. Quantum Chem.* **102**, 98 (2005); M. N. Huda and A. K. Ray (unpublished).
- <sup>46</sup>D. C. Wallace, *Phys. Rev. B* **58**, 15433 (1998).
- <sup>47</sup>T. Durakiewicz *et al.* (unpublished).
- <sup>48</sup>A. K. Ray and J. C. Boettger, *Phys. Rev. B* **70**, 085418 (2004); J. C. Boettger and A. K. Ray, *Int. J. Quantum Chem.* (to be published).
- <sup>49</sup>R. S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955); **23**, 1841 (1955); **23**, 2343 (1955).