

*Ab initio* CALCULATIONS FOR DISSOCIATIVE HYDROGEN ADSORPTION ON LITHIUM OXIDE SURFACES A. Sutjianto, S.W. Tam, L. Curtiss, and C.E. Johnson (Argonne National Laboratory) and R. Pandey (Michigan Technological University)

## OBJECTIVE

The objective of this work was to investigate dissociative hydrogen adsorption on lithium oxide surfaces. The surfaces were described using the so-called slab model, i.e., a finite number of atomic layers parallel to the exposed face.

## SUMMARY

Dissociative hydrogen chemisorption on the  $\text{Li}_2\text{O}$  surfaces of the (100), (110), and (111) planes has been investigated with *ab initio* Hartree-Fock calculations. Calculations for unrelaxed crystal  $\text{Li}_2\text{O}$  structures indicated that except for the (100) surface, the (110) and (111) surfaces are stable. Results on the heterolytic sites of n-layer (110) slabs (where  $n \geq 2$ ) and three-layer (111) slabs suggest that dissociative hydrogen chemisorption is endothermic. For a one-layer (110) slab at 100% surface coverage, the dissociative hydrogen chemisorption is exothermic, forming  $\text{OH}^-$  and  $\text{Li}^+\text{H}^-\text{Li}^+$ . This results also indicate that the low coordination environment in surface step structure, such as kinks and ledges, may play an important role in the hydrogen chemisorption process. On the homolytic sites of the (110) and (111) surfaces, there is no hydrogen chemisorption.

## PROGRESS AND STATUS

### Introduction

Lithium ceramics are a leading class of materials being considered as tritium breeders for fusion technology. Hydrogen is known to enhance the release of tritium from irradiated lithium ceramics. This "accelerator" role of hydrogen has been demonstrated in numerous in-pile experiments on tritium release [1-5]. The enhancement effect is usually accomplished by the addition of hydrogen (typically at a level of around 0.1%) to the helium purge gas. Despite this positive benefit, the use of hydrogen is not without problems. Chief among them are problems associated with tritium management via isotopic separation (due to the large hydrogen/tritium ratio) and tritium containment (arising from the presence of reduced form of tritium and the potential permeation loss).

To overcome these problems, one needs to gain an understanding of the mechanism through which hydrogen enhances tritium release. This knowledge would also benefit the search for alternative "accelerator" materials besides hydrogen. Therefore, we have initiated a program to investigate the process of hydrogen adsorption onto lithium oxide surfaces. This program combines an experimental component involving temperature programmed desorption with computer simulations that model the hydrogen adsorption process. This work reports the result of the computer simulation.

### Method

The technique that we have employed is the self-consistent-field Hartree-Fock linear combination of atomic orbital method modified to a crystalline environment. This *ab initio* method contains no *ad hoc* adjustable parameters and uses crystal orbital (COs) instead of molecular orbital (MOs). These COs are defined (similar to the quantum molecular approach) as a linear-combination of atomic orbitals but with the periodic environment of the crystal built in. This approach takes the extended nature of the crystalline materials into account. The CRYSTAL code [6] used for such calculationst has adopted this CO approach.

One of the keys to a successful *ab initio* calculation is obtaining a basis set that represents the electronic structure of the species. In the case of lithium oxide, its bonding characteristic is strongly ionic.

In free space, the  $O^{2-}$  is an unstable ion; however, in crystalline  $Li_2O$ , the anion is actually stabilized by the surrounding cation (in our case, lithium) environment. In this situation the two extra electrons on the oxygen ion would induce a relaxation of the valence electrons. This particular consideration for  $O^{2-}$  is necessary for any oxide that involves this oxygen ion in which the bonding is reasonably ionic. The effect is taken into account in an optimized basis set designed for the oxygen ion in a  $Li_2O$  environment [7]. Recent calculations on bulk crystalline  $Li_2O$  done by Dovesi, et al. [7] have indicated that the optimized basis set is able to give the lattice constant, bulk modulus, and elastic constant in good agreement with experimental values. We have therefore adopted this crystalline basis set [7] for our calculations involving lithium oxide. For the hydrogen, we have used the basis set obtained by Dovesi [8] where the calculated equilibrium Hartree-Fock bond length of  $H_2$  of 0.738 Å is in good agreement with its experimental value of 0.742 Å [9].

### Results and discussion [10]

The geometrical and electronic structures of the bulk  $Li_2O$ , the stability of the  $Li_2O$  surfaces, and dissociative hydrogen chemisorption on the  $Li_2O$  surfaces are discussed in the following sections.

#### Stability of unrelaxed $Li_2O$ crystal surfaces

The surface study was carried out with the slab model. In this model, the semi-infinite  $Li_2O$  crystal was simulated by a finite number of atomic layers parallel to the exposed face, reproducing the crystal geometry. Lithium oxide crystal has three surfaces, namely, (100), (110), and (111). The (100) surface consists of alternating lithium layers and oxygen layers. The distance between the two layers is 1.143 Å. Each layer of the (110) surface is neutral and has both lithium and oxygen on the same plane. The layer separation is 1.617 Å. The (111) planes, for the smallest neutral unit have two lithium layers with one oxygen layer. The distance between the lithium layer and the oxygen layer is 0.660 Å, and the distance between the two adjacent layers is 1.320 Å. The stacking of the layers for these different surfaces is represented in Fig 1.

Tasker [11] classified the charged layers into three classes, depending on the stacking sequences of the charged planes as one moves into the bulk of the crystal. The stacks of (100) planes are charged and have a dipole moment ( $\mu$ ) perpendicular to the planes (Fig. 1a). Addition of an extra neutral unit of two planes to the (100) surface creates dipole-dipole interaction, which will affect the energy of ions in the bulk crystal. The potential, therefore, never settles to its normal bulk value, and the surface energy does not converge. Thus, the (100) surface is energetically unstable and, therefore, will not be considered further in this work. Unlike the (100) planes, the (110) layers are built up from a stack of *neutral layers* (Fig. 1b). Both lithium and oxygen ions are present on each plane in a ratio such that the total charge is zero. The (110) surface is energetically stable since no dipole moment is created by the layer. Addition of (110) planes on the surface will have no electrostatic effect on an ion in the bulk. The (111) planes exhibit two different stackings. For one of these, the surface which terminates with the cation layer [Fig. 1c (i)] has no net dipole moment and is stable. The other, which starts with the anion layer [Fig. 1c (ii)], has a non-zero moment and causes the surface to be unstable. To our knowledge, no experimental study has been done on the ordering and facet properties of  $Li_2O$  surfaces. There has been an experimental study on the properties of (100) and (111) surfaces of  $UO_2$  (fluorite crystalline structure) determined by LEED (Low Energy Electron Diffraction) [12]. This study indicates that the (100) surface of uranium dioxide is also not stable.

The calculated surface energy of (111) and (110) surfaces is  $0.679 \text{ J m}^{-2}$  and  $1.443 \text{ J m}^{-2}$ , respectively. This reflects the fact that the (111) surface is the natural cleavage plane in the anti-fluorite structure. Although the (111) surface is energetically more favorable, in reality, one expects that a faceted  $Li_2O$  crystal would have both (110) and (111) surfaces present on a typical ceramic surface.

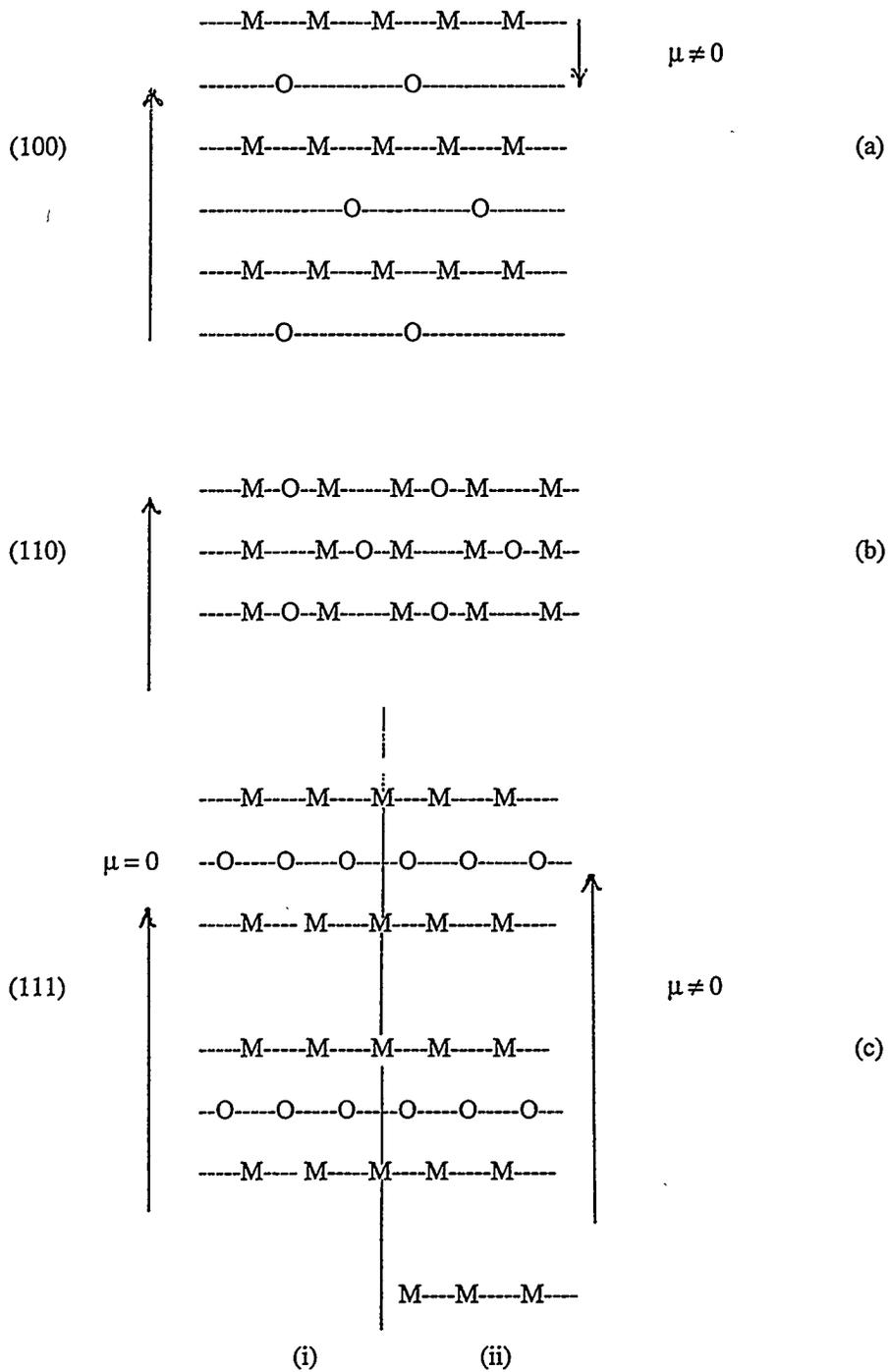


Figure 1. Stacking sequence of (100), (110), and (111) planes. The non-zero dipole moments ( $\mu$ ) occur on the (100) and (111) planes, with the anion termination. M denotes the  $\text{Li}^+$  and O is  $\text{O}^{2-}$ .

### Dissociative hydrogen chemisorption on the heterolytic site (110) and (111) terraces

Terraces are atomically flat planes on a crystalline surface and may terminate at structures called "steps". Two classes of adsorption sites are considered below: heterolytic sites, in this case Li-O sites, and homolytic sites, such as Li-Li and O-O sites.

Figs. 2 and 3 show a part of the extended top layer of the (110) terrace and the projection of the three (111) layers. To study H-H chemisorption on these terraces, we set up locations, within a unit cell, to place two hydrogen atoms. The unit cell of (110) and (111) surfaces is defined by the basis vectors ( $a_1, a_2$ ) and ( $b_1, b_2$ ) as shown in Figs. 2 and 3, respectively. The adsorption locations of the two hydrogen atoms being considered are also shown in these figures. Dissociative hydrogen sites are denoted by H(1)H(2), H(1)H(3), and H(1)H(4), where, for example, H(1)H(2) means that, at location 1, one of the hydrogen atoms is on top of oxygen and the other hydrogen is on top of lithium at location 2. Note that the model was set up such that the dissociative hydrogen appears only on top of surfaces; no hydrogen appears below the surfaces.

For each given H-H at a particular location, the calculations were done for one, two, and three (110) layers and for three (111) layers. Surface coverage of 100% and 50% were also considered for the n-layer slab (where  $n = 1, 2, \text{ and } 3$ ) for the (110) surface and 100%, 50% and 25% for the three-layer (111) surface. The 100% surface coverage means that each unit cell of the slab contains a dissociative hydrogen (H-H); 50%, and 25% surface coverage represent an H-H within each repeated cell that is two and four times larger than the original unit cell, respectively.

Heat of adsorption,  $E_{ch}$ , of the hydrogen at each reaction site is calculated by the following equation,

$$E_{ch} = E^n(\text{H-H}) - [E^n + E(\text{H}_2)], \quad (1)$$

where  $E^n(\text{H-H})$  represents the minimum total energy where dissociative hydrogen is chemisorbed at a given location (with the optimized  $h, d, \theta$  and  $s$ ) on the surface,  $E^n$  denotes the total energies of an n-layer slab, and  $E(\text{H}_2)$  denotes the energy of the free hydrogen molecule. The convention for Eq. (1) is as follows: if  $E_{ch}$  is negative, then the chemisorption is exothermic; if  $E_{ch}$  is positive, the chemisorption is endothermic.

### Heats of adsorption

Table 1 lists the calculated heat of adsorption at the given locations (Figs. 2 and 3) for the (110) and (111) terraces. As the number of layer increases from two to three layers, the H-H chemisorption energies on (110) surface, particularly at H(1)H(3), tend to become less endothermic. The heat of absorption of dissociative hydrogen at the given locations on four- and six-layer (110) slabs has also been studied. The calculated results indicate no further change of the adsorption energy for  $n \geq 3$ . Thus, all subsequent calculation are for the three-layer slab.

For a one-layer (110) slab as shown in Fig. 2, each anion is surrounded by four cations. This arrangement is of lower coordination when compared with six cations for each anion on a two-layer (110) slab. Consequently, a one-layer (110) slab is more reactive than slabs with more layers. Although a one-layer (110) slab is not a realistic model for a surface, this configuration could be used to understand the role of the lower coordination number of oxygen on surface step structures such as kinks and ledges. On a one-layer (110) slab with 100% surface coverage of H-H, the chemisorption state has an energy of -0.93 eV, for which one hydrogen attaches to the oxygen and the other hydrogen is attached between two lithiums (Fig. 2).

Table 1. The calculated Hartree-Fock LCAO-CO bondlengths  $d$  (Å) of dissociated hydrogen, located on top of the (110) and (111) surfaces (Figs. 2 and 3), and the heat of adsorption,  $E_{ch}$  (eV), for  $n = 1, 2$ , and 3 layers as obtained from CRYSTAL.

Li <sub>2</sub> O Surface	n	Locations of H	d(OH) Å	d(LiH) Å	d(H-H) Å	$E_{ch}$ eV
(110) [Figure 2]						
	1	H(1)H(2)	0.96	1.54	2.06	0.94
		H(1)H(3)	0.96	1.59	2.08	-0.93
		H(1)H(4)	0.96	2.04	2.33	-0.64
	2	H(1)H(2)	0.98 (0.97)	1.57 (1.57)	2.07 (2.07)	1.71 (2.27)
		H(1)H(3)	0.96 (0.96)	1.69 (1.73)	2.89 (2.90)	0.57 (1.02)
		H(1)H(4)	0.96 (0.96)	2.20 (2.21)	2.60 (2.60)	0.86 (1.43)
	3	H(1)H(2)	0.97 (0.97)	1.57 (1.58)	2.07 (2.07)	1.54 (1.82)
		H(1)H(3)	0.96 (0.96)	1.65 (1.72)	2.88 (2.90)	0.33 (0.79)
		H(1)H(4)	0.96 (0.96)	2.18 (2.21)	2.59 (2.61)	0.61 (1.05)
(111) [Figure 3]						
	3	H(1)H(2)	1.1 (1.0) [1.0]	1.48 (1.55) [1.70]	2.14 (2.17) [2.31]	3.65 (2.96) [2.70]
		H(1)H(3)	1.0 (1.0) [1.0]	1.60 (1.60) [1.65]	2.77 (2.77) [2.80]	3.24 (2.24) [1.95]
		H(1)H(4)	1.0 (1.0) [1.0]	2.22 (2.25) [2.33]	1.27 (1.30) [1.41]	2.73 (2.10) [1.74]

\* The calculated adsorption energies are listed for various surface coverages. For 25%, 50%, and 100% surface coverages are represented by the data in the square bracket, bracket, and without bracket, respectively.

### Electronic structure

Fig. 4 illustrates the density of states (DOS) for a one-layer slab of (110) surface, and 100% surface coverage, before and after chemisorption. Before chemisorption (finer lines), the uppermost valence bands are the O 2p bands indicated by the three peaks (denoting  $2p_x$ ,  $2p_y$  and  $2p_z$  bands). The O  $2p_z$  plays the key role in the interaction with the hydrogen.

The thicker lines in Fig. 4 are the DOS in the presence of dissociative hydrogen at H(1)H(3) (see Fig. 2). In the dissociative chemisorption state, the O 2s band is stabilized downward by a band shift of about 4.5 eV. For the O 2p bands, the  $2p_x$  and  $2p_y$  bands are also shifted by about 3.58 eV. The narrow band between -16.770 and -16.410 eV represents the formation of  $\text{OH}^-$  as a result of overlapping between the O  $2p_z$  and H 1s orbital. There is no contribution from the  $2p_x$  and  $2p_y$  orbital in the O-H bond. A gap of 1.2 eV is created between the  $2p_z$  and both the  $2p_x$  and  $2p_y$  bands. The band that lies between -9.470 and -7.960 eV represents the H that bonds with the two cations in the form of  $\text{Li}^+\text{HLi}^+$ .

The electronic charge densities of the  $\text{OH}^-$  and  $\text{Li}^+\text{HLi}^+$  are shown in Figs. 5 and 6. A strong bond appears for  $\text{OH}^-$  with a very localized electronic charge density, while for  $\text{Li}^+\text{HLi}^+$  the bonding is more ionic, with a clear-cut charge separation between  $\text{Li}^+$  and H. The OH and LiH bond lengths are 0.96 and 1.54 Å, respectively, which are closely comparable with the OH (0.97 Å) and LiH (1.595 Å) bond lengths reported for the gas phase[9]. For lower coverage (50%) on a one-layer (110) slab, endothermic H-H chemisorption occurs. This means that the exothermic dissociative hydrogen chemisorption at 100% coverage may be due to the lower coordination of the Li-O site or to nearest neighbor adsorbate-adsorbate interactions.

Results from the n-layer (110) slab (where  $n = 2$  and 3) with 100% surface coverage suggest that its H-H chemisorption is endothermic. The density of states for the O 2p band of the (110) surface in the one-, two-, and three-layer systems (Fig. 7) indicates that the O 2p band stabilizes as additional layers are introduced. For example, in the case of two- and three-layers, the O 2p band shifts are about 2 and 2.6 eV, respectively, relative to the upper-limit O 2p band of a one-layer slab. This means that as more layers are introduced to the surface, the surface becomes more stable, as expected. Lower surface coverage (50%) also exhibits endothermic chemisorption (Table 1).

For the (111) surface, the O 2p band lies in the range close to the O 2p band of a one-layer (110) slab, at -10.638 to -8.086 eV. However, only endothermic hydrogen chemisorption occurs on the (111) surface. One reason is screening of the lithium layers; as a result, it is energetically unfavorable for the  $\text{H}^+$  to move close to the positively charged  $\text{Li}^+$  layer before it can be chemisorbed by the  $\text{O}^{2-}$ .

### Dissociative hydrogen chemisorption on the homolytic site (110) and (111) terraces

Calculations for the homolytic sites of the terrace, such as, Li-Li and O-O, indicate no H-H chemisorption. For H-H chemisorption to occur on the homolytic sites, it has to be in the form of either two  $\text{H}^+$  or two  $\text{H}^-$  ions, where each hydrogen attaches to two oxygens or to two lithiums. For the O-O site, each oxygen would have to release its valence electron, or each hydrogen would have to release its electron to the crystal environment, and the released electrons would have to be captured by the cations, forming neutral lithiums. For the Li-Li site, each hydrogen would need to capture an electron from oxygen to form  $\text{H}^-$  while the anion becomes  $\text{O}^-$ . Such phenomena do not occur for the  $\text{Li}_2\text{O}$  surface under equilibrium conditions since they require transferring electrons into the surrounding crystal environment. This is equivalent to creation of electronic defects, (for example, neutral Li or  $\text{O}^-$ ). The surface band structure that we have obtained indicates that electronic disorder is energetically unfavorable. It is possible that electronic defects may occur under highly non-equilibrium conditions, such as irradiation, which creates electronic structure defects on the crystal surface. However, at equilibrium no homolytic chemisorption occurs.

### Summary

Dissociative hydrogen chemisorption on the (110) and (111) terraces has been studied with the *ab initio* Hartree-Fock technique. Both the finite cluster and extended crystalline models qualitatively agree that endothermic dissociative hydrogen chemisorption occurs on these terraces. The calculations for the (110) terraces in the n-layer slab model (where  $n = 2$  and  $3$ ), indicate a metastable chemisorption at heterolytic sites and no chemisorption at the homolytic sites. Exothermic chemisorption with 100% coverage takes place for the case of a one-layer (110) slab around the Li-O site. This is caused by the lower coordination of the oxygen and nearest neighbor adsorbate-adsorbate interactions. Although a one-layer (110) slab represents an unphysical surface, this model illustrates that a lower coordination environment, as in surface step structures such as kinks and ledges, may play an important role in the hydrogen chemisorption process. This will be investigated in the next state of our work. Although the oxygen (111) terrace has the same local coordination and similar energy range of O 2p orbital as it does in the (110) terrace, there is only endothermic hydrogen chemisorption.

### FUTURE WORK

A number of approximations used in this study should be noted. First, correlation effects, which can be important in bond breaking and making, were not included. Second, more polarization functions may need to be introduced, particularly, along the bonding between surface site and hydrogen. Third, local relaxation of the surface was not considered. Future studies will take consideration of these effects, as well as use of other types of basis sets, which may give an improved account of bond energetics.

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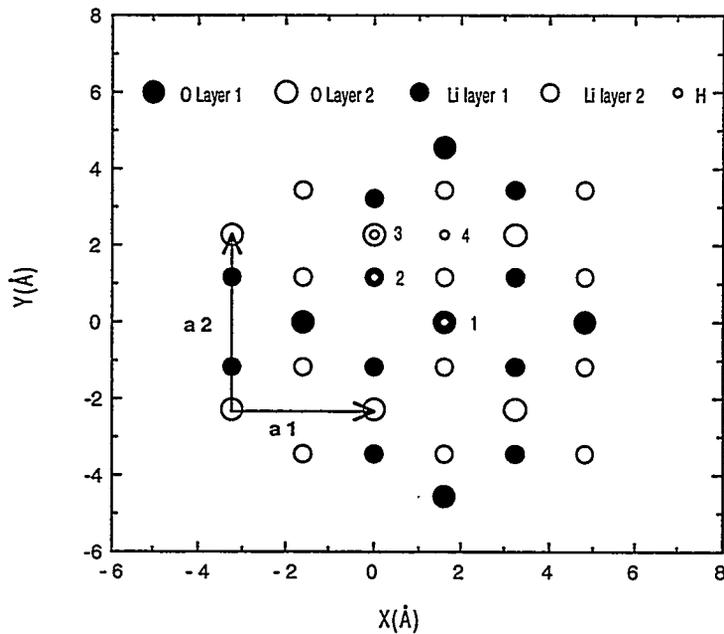


Figure 2. Geometry of the two-layer (110) slab. The unit cell is defined by basis vectors  $a_1 = (3.23, 0.0, 0.0)$  Å and  $a_2 = (0.0, 4.57, 0.0)$  Å. The locations of dissociative hydrogen are represented by 1, 2, 3, and 4.

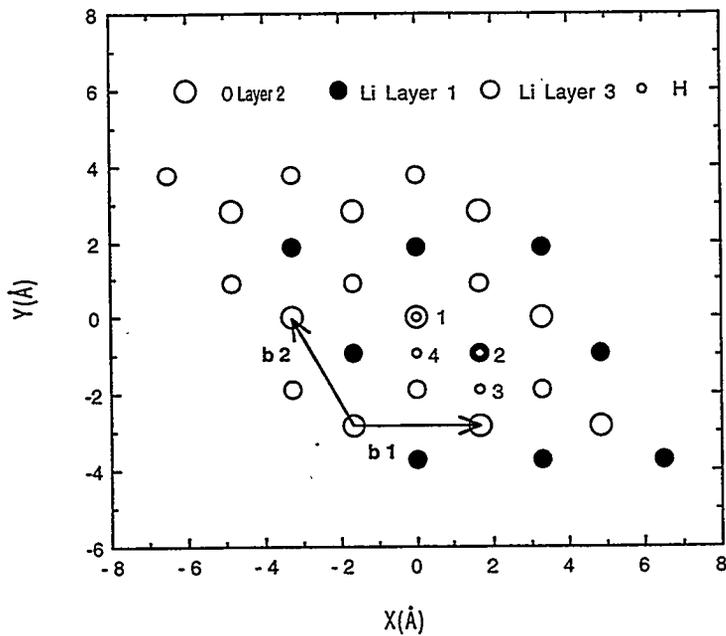


Figure 3. Geometry of the three-layer (111) slab. The unit cell is defined by basis vectors  $b_1 = (3.23, 0.0, 0.0)$  Å and  $b_2 = (-1.62, 1.87, 0.0)$  Å. The locations of and 4.

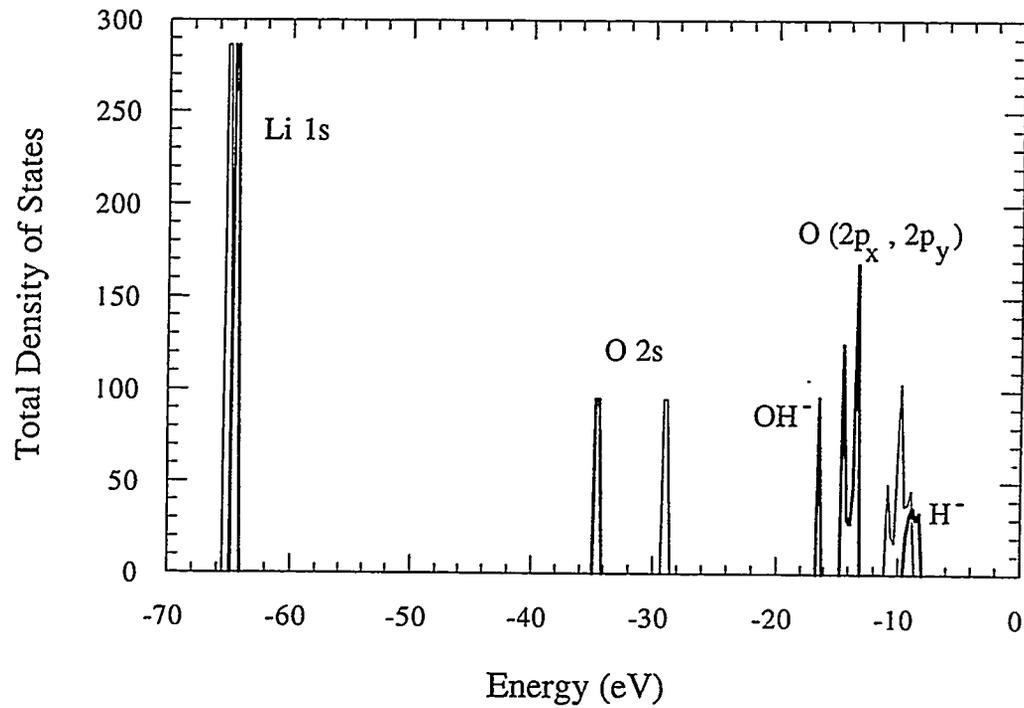


Figure 4. Density of states for a one-layer (110) slab. Before chemisorption is represented by the finer lines. The thicker lines represent the DOS where dissociative hydrogen is chemisorbed.

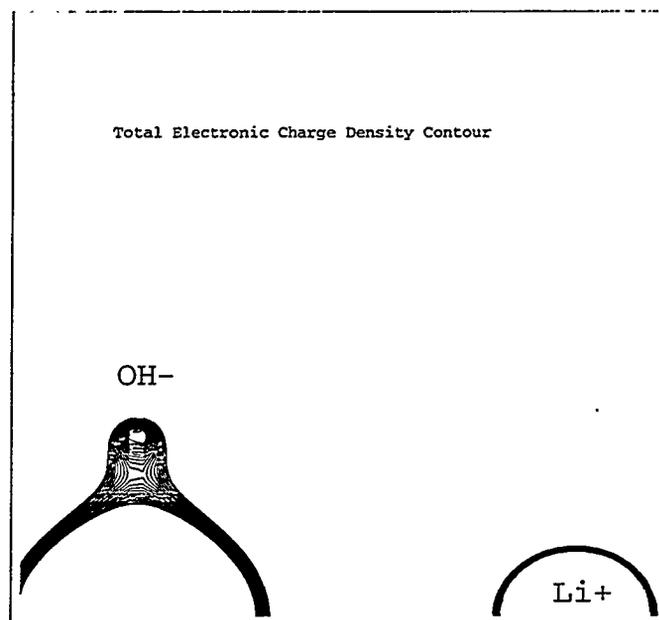


Figure 5. Total electronic charge density map of the  $\text{OH}^-$  bond on a one-layer (110) slab with the contour interval of  $0.003 \text{ \AA}$ .

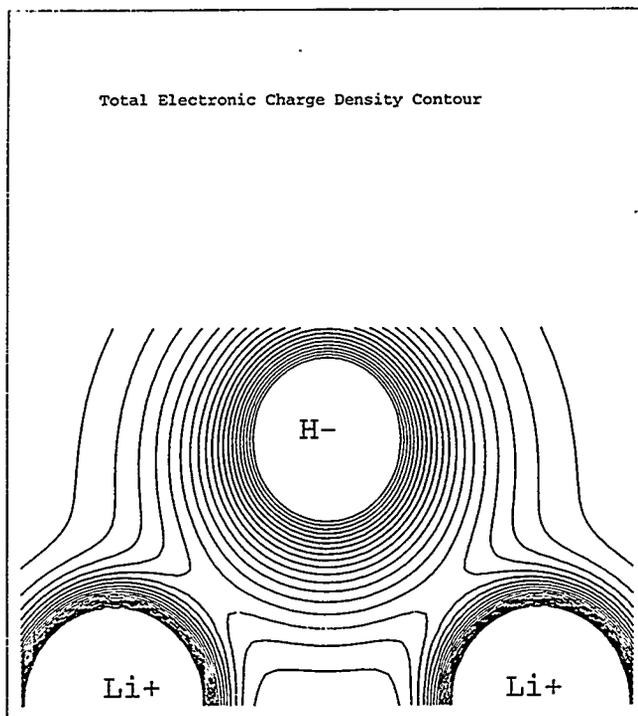


Figure 6. Total electronic charge density map of the ionic bonding of  $\text{Li}^+\text{HLi}^+$  on a one-layer (110) slab.

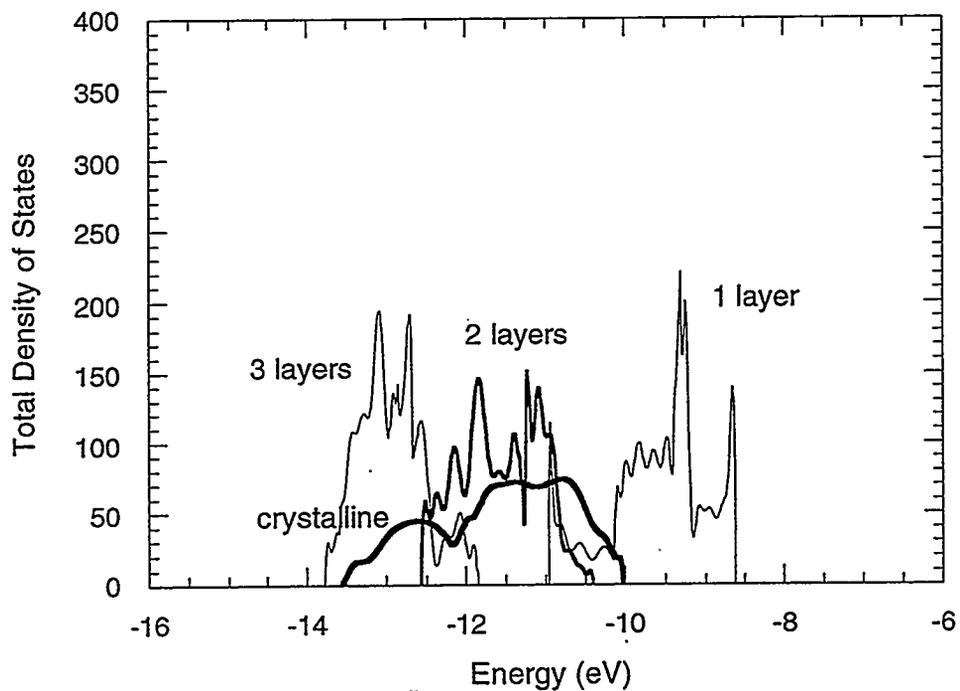


Figure 7. Schematic diagram of the total density of states of O 2p for the one-, two- and three-layer slab of the (110) surfaces.