A local density functional investigation of the clean and the hydrogen covered Li(001) surface

U. Birkenheuer a, J.C. Boettger b, N. Rösch a,∗

a Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany
b Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Received 8 April 1995; accepted for publication 30 June 1995

Abstract

A detailed density functional theory study on periodic slab models of the clean and the hydrogen covered Li(001) surface is presented to corroborate recent experiments on atomic hydrogen adsorption at lithium surfaces. Questions of model convergence as well as the bonding mechanism in the adsorption system are investigated. Several tools are employed to analyze the self-consistently determined electronic structure of the Li(001) and H/Li(001) slab models, among them one-particle core level shifts, overlap populations and density difference maps. To quantify the charge separation within the ionic surface layer formed in the H/Li(001) adsorption system, the topological atom approach and a recently developed technique uniquely based on the electrostatic potential above the surface are used. Lithium is found to behave to some extent like a covalent solid rather than an s electron metal, while the adsorption system H/Li at full monolayer coverage is best characterized by an insulator–metal interface.

Keywords: Alkali metals; Chemisorption; Density functional calculations; Hydrogen; Low index single crystal surfaces

1. Introduction

Lithium, like Mg, Pt, Pd and other metals, shows a strong tendency to absorb large amounts of hydrogen [1]. It may therefore be of great technical importance in connection with the transport of energy from solar power stations. Yet, there exist only few experimental data on the initial step of absorption into bulk lithium, i.e. on the adsorption of hydrogen at a lithium surface. Recently, in an extension of a series of experiments on the adsorption of hydrogen on surfaces of simple metals, like Be [2], Na [3], Mg [4], Al [3,5], and K [6], the lithium surface was investigated too [7].

On the other hand, the adsorption of hydrogen on lithium has been a popular subject among theoreticians despite this scarcity of experimental data. Examples of such studies are jellium-type investigations (some of them including weak pseudopotentials to simulate the substrate atoms) [8–11], a number of configuration interaction (CI) calculations based on cluster models [12–18] and a recent HF (Hartree–Fock) study [19] using periodic slab models for different hydrogen coverages. Clearly, this popularity is connected to the fact that the adsorption system H/Li comprises the lightest of all metal substrates and the simplest adsorbate, atomic hydrogen. Therefore, it is often chosen as the first proving ground for a new computational method. Flores and co-workers

0039-6028/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0039-6028 (95) 00753-9
[20] used H/Li to calibrate a new model Hamiltonian using “ab initio” results [21], similarly Ravenek and Geurts [22] employed it to test their Hartree–Fock–Slater cluster-in-cluster implementation of the moderately large embedded cluster (MLEC) formalism [23]. The first implementation of the MLEC technique in the framework of density functional theory (DFT) employing a periodic substrate [24] was also devoted to the investigation of atomic hydrogen adsorbed on a lithium surface [25,26]. Similar calculations have been performed by Pisani and co-worker [19] to check the applicability of a new embedding formalism [27] to metallic substrates.

In the present study the clean and the hydrogen covered lithium surface is re-investigated within DFT using slab models. For this purpose, the FILMS program package [28,29] was employed which recently has been significantly improved [30,31]. This program is a full-potential, all-electron DF implementation for 2D (two-dimensional) periodic slabs based on the LCGTO–FF technique. In the latter strategy the Kohn–Sham wave functions as well as the electron density and the exchange–correlation (XC) potential are represented as linear combinations of Gaussian-type orbitals (LCGTO), the latter two quantities by fitting functions (FF). One purpose of this investigation was to cross-check our recent MLEC-DF embedding study on an isolated hydrogen atom adsorbed on Li(001) [25,26] which was based on the LCGTO-DF cluster method [32]. Two methodological questions are of immediate interest, when comparing results obtained with slab models to those of embedded cluster calculations, namely how large a 2D supercell should be to essentially describe a single-atom adsorption process and how many layers a slab model should comprise to reach convergence.

However, the main goal of the present work was to provide physical and chemical insight into the chemisorption process taking place when atomic hydrogen interacts with a clean lithium surface. Therefore not only typical adsorption observables, like adsorption height, binding energy, vibrational frequency and induced work function change, will be discussed, but also a detailed analysis of the one-particle spectra (band structure) and of the charge distribution within the model slabs will be given. We have applied the topological atom analysis [33,34] as well as a recently developed tool to examine the degree of ionicity of a surface [30,35] which is based on a Fourier expansion of the electrostatic field above the surface. After a brief description of the computational details in the next section, we will start the presentation in Section 3 with the clean Li(001) surface to allow for a separate discussion of the typical substrate features. Section 4 is then devoted to the adsorption process itself.

2. Computational details

The geometrical details of the various slab models will be discussed later on in Sections 3 and 4. Here, we focus on the choice of the basis sets and on other computational parameters which control the quality of the calculation. The orbital basis set was generated by contracting reasonably large Gaussian-type basis sets for lithium [36] and hydrogen [37] using atomic eigenvectors, obtained from non spin-polarized LDA calculations, Li (9s, 4p)→[4s, 2p], and H (6s, 1p)→[3s, 1p]. These basis sets have proven sufficiently flexible in previous MLEC-DF cluster embedding studies [24–26]. For the construction of the fitting basis sets, used to represent the electronic charge and the XC potential, we followed the same scheme which we found well suited in previous FILMS investigations [30,35] and which relies on modified even-tempered expansions:

\[ \alpha_n = \alpha_{\text{min}} (\alpha_{\text{max}}/\alpha_{\text{min}})^{n/N} \left( q^{(N-n)/(2N-2)} \right), \]

\[ n = 0, 1, \ldots, N. \] (1)

The construction principle of this expansion is to have the incremental factors \( \lambda_n = \alpha_n/\alpha_{n-1} \) between successive exponents (which are constant in even-tempered expansions [38]) decrease for the more diffuse fitting functions of the valence region. The ratio \( q = \lambda_1/\lambda_N \) between the first and last incremental factor was set to 0.5. The most diffuse and the tightest s exponents, \( \alpha_{\text{min}} \) and \( \alpha_{\text{max}} \), were obtained by scaling the corresponding orbital exponents [39]. However, the most diffuse s-type exponents (charge density: 0.0474, exchange–correlation, XC,
potential: 0.0158) were dropped to avoid numerical instabilities in the computed slab work function, which could otherwise originate from slightly negative densities in the fitted charge density outside the slab. The exponents of the polarization fitting functions (p- and d-type) were chosen to be proportional to the s-type exponents and fixed such that the radial maxima of the most diffuse polarization functions are located at the bond centers. It was found that a (11s,2p,2d) basis set for Li and a (6s,3p,1d) basis set for H was necessary to assure a sufficiently flexible representation of the fitted quantities. The orbital as well as the fitting basis sets showed no indications of approximate linear dependence in all the calculations of this study.

For the local density (LD) approximation to the xc potential the parametrization of Vosko et al. [40] was chosen. The k-space integration was performed within the 2D analogue of the tetrahedron method [41]. To avoid discrepancies in the accuracy of the discrete k-space integration for the various overlayers investigated (for details see Section 4), the triangulation of the irreducible wedges of the different 2D Brillouin zones were constructed so that the triangles of the smaller wedges \([p(2 \times 2)<c(2 \times 2)<p(1 \times 1)]\) exactly match the triangles of the next larger one. We decided to use 15 irreducible k-points for the \(p(1 \times 1)\) structure after we found that the total energy of lithium slabs of up to five layers changed by less than 0.05 eV when the number of irreducible k-points was increased from 15 to 28. The changes in the work function were even smaller (<0.03 eV). No multiple expansions are embodied in the FILMS program; instead, a generalized Ewald technique is used to evaluate the long range Coulomb integrals [31]. The cutoff criterion for the internal lattice sums was set to a relative precision of \(3 \times 10^{-12}\) for each matrix element.

3. The clean Li(001) surface

Under normal pressure crystalline lithium exists in two different modifications. For temperatures near absolute zero its crystal structure is hexagonal closed packed (hcp phase), while for temperatures above 72 K it passes into a bcc (body centered cubic) phase [42]. Plummer and co-workers carried out their experiment on hydrogen adsorption on lithium [7] for temperatures above 100 K. Furthermore, except for two investigations of Hira and Ray [15,17] where lithium is assumed to take a cubic closed packed crystal structure (fcc phase), all previously mentioned theoretical studies of H/Li refer to lithium in its bcc phase. To allow for a direct comparison with the results of the MLEC-DF study [24–26] the four-fold bcc (001) surface of lithium was considered, although the bcc (110) surface may be more stable because of its smaller surface unit cell compared to the quadratic bcc (001) one. The (001) surface is modeled by periodically extended 2D slab models of up to seven lithium layers, using the experimental lattice parameter, \(a=3.49\) Å [43]. Results of a previous FILMS study [29] on thin hexagonal lithium films are also taken into account for the discussion of the binding energy.

The following analysis of the electronic structure of the clean lithium surface focuses on the charge distribution within the substrate and on the influence of the (001) surface on the bulk properties of lithium. In addition, we will look for possible quantum size effects in thin metal layers, extending previous studies of Al(111) films [44] and films of Li in its low-temperature hcp phase [29].

3.1. Slab convergence

Because of the metallic character of lithium, one may expect that the influence of its surfaces will be noticeable for quite a few crystal layers inside the lithium crystal. Thus the question arises of how many crystal layers a model slab should comprise so that its inner layers will exhibit typical bulk-like behavior. The first quantity to be examined in this respect is the cohesive or binding energy per 2D unit cell of Li(001) \(n\)-layer systems, defined as

\[ E_{\text{coh}}(n) = nE_{\text{tot}}(\text{Li}) - E_{\text{tot}}(\text{Li}(001)). \]

The atomic reference energy \(E_{\text{tot}}(\text{Li}) = -199.83\) eV was obtained in a spin-polarized LDF calculation using the same orbital basis set. For sufficiently thick slab models, convergence to the bulk is anticipated to result in a linear variation of \(E_{\text{coh}}(n)\)
with the number \( n \) of layers:

\[
E_{\text{coh}}(n) = nE_{\text{bulk}} - 2E_{\text{surf}},
\]

where the coefficients \( E_{\text{bulk}} \) and \( E_{\text{surf}} \) may be interpreted as values for the bulk cohesive energy per 3D unit cell and the surface energy per 2D unit cell, respectively (Table 1). This approximately linear behavior is already discernible in the layer-by-layer increments \( E_{\text{inc}}(n) = E_{\text{coh}}(n) - E_{\text{coh}}(n-1) \) of the cohesive energies which vary only within the small range from 1.68 to 1.81 eV for the whole range of slabs from one up to seven crystal layers. More clearly, it may be seen from a comparison of the calculated cohesive energies with the results \( E_{\text{reg}} \) from at least-squares fit to \( E_{\text{coh}}(n) \) (Table 1). The deviations \( E_{\text{diff}} = E_{\text{coh}} - E_{\text{reg}} \) are very small, ±0.03 eV. When this type of analysis is applied to recently published data for the cohesive energies of model slabs of up to five layers for the hexagonal (0001) surface of lithium [29], an almost perfect linear dependence of the cohesive energy on the number of crystal layers is found for this surface as well (Table 1), with a mean squared deviation of the corresponding linear regression amounting to 0.02 eV. These findings are in remarkable contrast to the results of free-electron metals, e.g. for Al(111) [44–46]. There, the slab cohesive energy was found to vary linearly only for slabs of four layers and more, whereas for lithium this linear behavior extends down to a monolayer. A similar observation has been made for the highly ionic MgO(001) surface [30,35]. The linear variation of the cohesive energy may be regarded as a first indication for the fact that, even though lithium is a metal, the influence of the (001) surface on the Li crystal is essentially confined to the top surface layer. HF calculations [19] for Li(001) slabs of up to five layers support these findings. There, only the cohesive energy of the bi-layer was found to deviate by 0.34 eV from the otherwise perfect linear behavior (mean squared deviation 0.02 eV).

Using Eq. (3) a bulk cohesive energy \( E_{\text{bulk}} \) of 1.76 eV and a surface energy \( E_{\text{surf}} \) of 0.43 eV is derived from Li(001) slab models. The corresponding values for the Li(0001) surface [29] are 1.62 and 0.25 eV, respectively. In Table 2 these energies are compared to the results of LDF bulk calculations and to experimental data. It is well-known from previous bulk studies (see Refs. [47–49], and references therein) that the total LDF energy of crystalline lithium significantly depends on the parametrization chosen to approximate the local XC potential. Except for the present study where the parametrization of Vosko et al. [40] was used, the theoretical results reported in the Table 2 were obtained with the XC approximation proposed by Hedin and Lundqvist [50]. Taking into account these differences in methodology and in the basis sets employed, the computed bulk energies for the two different crystalline lithium phases are quite close to each other. The agreement with the experimental data is also remarkable. Compared to the experimental value of 1.64–1.66 eV for the bulk cohesive energies the LDF calculations overesti-

### Table 1

Calculated LDF cohesive energy \( E_{\text{coh}} \) per 2D unit cell of Li(001) (bcc phase) and Li(0001) (hcp phase) slabs of up to seven layers.

<table>
<thead>
<tr>
<th>( n )</th>
<th>Li(001) – bcc phase</th>
<th>Li(0001) – hcp phase&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_{\text{coh}} )</td>
<td>( E_{\text{inc}} )</td>
</tr>
<tr>
<td>1</td>
<td>0.94</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>2.62</td>
<td>2.65</td>
</tr>
<tr>
<td>3</td>
<td>4.18</td>
<td>4.41</td>
</tr>
<tr>
<td>4</td>
<td>6.19</td>
<td>6.16</td>
</tr>
<tr>
<td>5</td>
<td>7.89</td>
<td>7.92</td>
</tr>
<tr>
<td>7</td>
<td>11.45</td>
<td>11.43</td>
</tr>
</tbody>
</table>

<sup>a</sup> Using the binding energy per Li atom reported in Ref. [29].

Also shown are the incremental energies \( E_{\text{inc}}(n) = E_{\text{coh}}(n) - E_{\text{coh}}(n-1) \), the results \( E_{\text{reg}} \) of a linear regression of the cohesive energy versus the number \( n \) of layers in the slab models and their deviation \( E_{\text{diff}} = E_{\text{coh}} - E_{\text{reg}} \) from the calculated cohesive energies \( E_{\text{coh}} \). All energies are given in eV. The atomic reference energy of lithium is –199.83 eV.
Table 2
Comparison between theoretical and experimental values of the bulk cohesive ($E_{\text{bulk}}$) and surface ($E_{\text{surf}}$) energies (in eV) for the two lithium surfaces bcc (001) and hcp (0001)

<table>
<thead>
<tr>
<th>Method</th>
<th>Li(001) – bcc phase</th>
<th>Li(0001) – hcp phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{bulk}}$</td>
<td>$E_{\text{surf}}$</td>
</tr>
<tr>
<td>2D band structure calculation</td>
<td>1.76</td>
<td>0.43</td>
</tr>
<tr>
<td>3D band structure calculation</td>
<td>1.73$^c$</td>
<td>1.62$^a$</td>
</tr>
<tr>
<td>Experimental values</td>
<td>1.66$^d$</td>
<td>1.69$^b$</td>
</tr>
<tr>
<td></td>
<td>1.66$^d$</td>
<td>1.73$^c$</td>
</tr>
<tr>
<td></td>
<td>1.66$^d$</td>
<td>1.66$^c$</td>
</tr>
<tr>
<td></td>
<td>1.64$^h$</td>
<td>0.25$^a$</td>
</tr>
</tbody>
</table>

* Based on the values reported in Ref. [29]. $^b$ Ref. [47] (LCGTO method). $^c$ Ref. [49] (FLAPW method) estimated, using the atomic energy of Li given in Ref. [29]. $^d$ Ref. [73]. $^e$ Ref. [52]. $^f$ Ref. [74]. $^g$ Ref. [53]. $^h$ Ref. [75] (phase not specified). The energies for the bcc phase are from the present LDF calculations using the Vosko–Wilk–Nusair parametrization of the local density approach to the exchange-correlation potential. All other theoretical results are based on LDF calculations employing the Hedin–Lundqvist parametrization of the exchange-correlation potential. The slab calculations were performed with the FILMS program package (LCGTO-FF method), the methods employed for the bulk calculations are indicated separately.

mate the binding energy by only about 0.1 eV (Table 2). This difference is comparable in magnitude to that found for the binding energy of the Li dimer where a molecular calculation using the same orbital basis set and the same XC potential yields 1.00 eV compared to the experimental value of 1.04 eV [51]. The agreement between the calculated results for the surface energy and the corresponding experimental values, 0.40 eV per unit cell for the bcc (001) surface [52] and 0.26 eV per unit cell for the closer packed hcp (0001) surface [53], is even better. They differ by just 0.03 eV for the bcc (001) and 0.01 eV for the hcp (0001) surface (Table 2).

The linear behavior described by Eq. (3) indicates a very short range for the influence of the surface on the underlying Li crystal. Therefore it seems worth analyzing this effect in more detail. A suitable, local and very sensitive probe for the surface influence are core level shifts [54]. Although LDF one-particle core level energies are not directly comparable to experimental core ionization energies, they provide a useful and simple theoretical quantity to analyze differences in the chemical or physical environment. In this sense, the one-particle Li 1s core level energies of the various atoms in the Li(001) slab systems are compared to each other in Table 3. To facilitate this comparison, the values are given relative to the Fermi level of each slab system.

Table 3
Calculated Li 1s core level energies (in eV) relative to the Fermi level, $E_{\text{Li}}-E_{\text{F}}$, and the work function $\Phi = -\Delta E_{\text{F}}$ of Li(001) slabs of up to seven layers

<table>
<thead>
<tr>
<th>Layers</th>
<th>$\Phi$</th>
<th>Relative Li 1s core level energies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Li(1)</td>
</tr>
<tr>
<td>1</td>
<td>3.28</td>
<td>47.31</td>
</tr>
<tr>
<td>2</td>
<td>3.05</td>
<td>46.62</td>
</tr>
<tr>
<td>3</td>
<td>2.93</td>
<td>-46.39</td>
</tr>
<tr>
<td>4</td>
<td>3.11</td>
<td>-46.60</td>
</tr>
<tr>
<td>5</td>
<td>2.96</td>
<td>-46.53</td>
</tr>
<tr>
<td>7</td>
<td>3.09</td>
<td>-46.54</td>
</tr>
<tr>
<td>Exp.</td>
<td>2.9$^a$</td>
<td></td>
</tr>
</tbody>
</table>

* Ref. [69].

Li(j) indicates the atoms in the jth surface or sub-surface layer. The atomic 1s core level energy of lithium was calculated as $-51.11$ eV.

The relative 1s core level energies of the subsurface atoms Li(2) to Li(4) (Table 3) are practically identical (−45.90 to −45.81 eV), and thus corroborate that already within the first (001) subsurface layer the Li atoms experience an essentially bulk-like environment. A similar conclusion on the layer convergence may be derived from the core level energies of the top-layer Li atoms Li(1) (Table 3). Their relative energies, except for a slight upward trend, exhibit no significant changes, when passing from the bi-layer to the seven-layer Li(001).
slab. Thus the influence of the sub-surface Li atoms on the surface crystal layer seems to be already converged for a bi-layer slab. Similar results were found for the one-particle energies of a periodic HF calculation [19]. Although the fluctuations are somewhat larger, \(\pm 0.3\) eV, than those of the Kohn–Sham one-particle core level energies, the general trends are similar to those discernible from Table 3.

### 3.2. The charge distribution in Li(001)

The topological atom analysis provides an interesting alternative to simple charge density or density difference maps [33,34]. Thereby one subdivides space into disjunct regions via the zero-flux surfaces of the density gradient field of the total charge density. The regions constructed in this way are the basins of each of the local maxima of the total electronic density, acting as attractors of the gradient field. Since in a wide variety of systems the only local maxima are located at the atomic centers (the nuclear attractors) [55] this technique provides a purely topological definition of well-shaped atoms in atomic aggregates. Only very few systems, e.g. the dimers Li\(_2\), C\(_2\) and Be\(_2\) and their positive ions, are known to exhibit non-nuclear attractors in their density [55]. Speculations [56] that these particular local maxima might be an artifact of the underlying HF derived density were not confirmed: the analysis of the electron distributions in planar Li clusters [57], based on CI wave functions [58,59], has identified non-nuclear attractors as an intrinsic property of Li clusters, which may be closely related to the well-known tendency of lithium to form so-called three-center bonds. Planar Na clusters are another example of systems with non-nuclear attractors in their correlated electron density [60].

Stimulated by these observations based on finite clusters, it seemed worthwhile to apply the topological atom analysis to the DFT charge density of the extended 2D slab models of lithium calculated with the FILMS program package. In Fig. 1 the result is shown for the case of a five-layer Li(001) model slab. The shape of the contours (dashed and dotted lines) and of the boundaries of the “topological atoms” (solid lines) is typical for each of the investigated slab models. One of the most interesting features in Fig. 1 are the non-nuclear attractors outside the Li “atoms” (marked by crosses). They can be found in each interstitial region between three Li atoms and thus provide direct evidence for three-center bonds in Li aggregates. However, one should keep in mind that the charge density in the interstitial region of the Li(001) slab models is extremely flat. In the case of the five-layer slab displayed in Fig. 1, for example, the value of the electron density at the non-nuclear attractors between the first and second crystal plane amounts to \(8.2 \times 10^{-3}\) au and at those between the second and third crystal plane to \(7.7 \times 10^{-3}\) au, only a few percent higher than at the neighboring local minima. This is very similar to the findings for correlated electron distributions of planar Li clusters [57].

Another interesting detail of Fig. 1 are the contours of the total density outside the Li(001) model slab. Just a few ångström above the top crystal plane almost no corrugation is discernible in the electron distribution. This may be regarded as a
first indication for a profound charge transfer from outside the (001) surface into the four-fold hollow sites in the first crystal plane. To corroborate this diagnosis, density difference maps of the Li(001) surface were generated by subtracting a superimposition of atomic Li charge densities from the self-consistent charge distribution computed for the model slabs. As a characteristic example the density difference map of a seven-layer is shown in Fig. 2. The charge transfer just mentioned is clearly discernible. The formation of the three-center bonds is also visible in the charge density difference. The electron charge density in the interstitial region is not accumulated in the region between next-nearest Li neighbors (along the [111] direction), but in the center of each of the distorted Li octahedra of the bcc crystal structure (see Fig. 2). The most striking feature of the charge density difference, however, is the pronounced band of negative charge between the surface and the sub-surface Li layers (Fig. 2). This accumulation of electron charge density may be linked to the tendency of Li to form three-center bonds. While Li atoms in the interior of a slab may form three-center bonds to both sides of their crystal plane, for atoms of the top surface layer only the sub-surface atoms are available as partners. Hence an electron transfer from the top-layer atoms into the interstitial region between the top two crystal planes occurs, resulting in the observed sub-surface band of electron charge accumulation. The fact that these surface induced structures are confined to the first two substrate layers is consistent with the finite range of the (001) surface influence discussed in the previous section.

3.3. The surface dipole of Li(001)

According to calculations using the jellium model of the free electron gas [61] metal surfaces should exhibit a slight electron transfer into the vacuum region, the so-called electron spill-over. Thus, the surfaces of such metals should be characterized by a surface dipole moment pointing into the bulk. In this sense, lithium does not behave like a typical free-electron metal. Due to its rather unusual charge distribution (see Fig. 2) a dipole moment pointing away from the bulk is expected for the bcc (001) surface of lithium, mainly due to the closed band of negative charge density between the top two crystal planes (see above). Because of the (glide-) mirror plane symmetry of the Li(001) slab models, however, this dipole moment cannot be calculated directly. Attempts to quantify it as half space dipole moment strongly depend on the arbitrary choice of the cutting plane between the atomic layers inside the slab.

An alternative, though only indirect access to the polarization of the surface layer is provided by the 1s core level shifts of the Li atoms in the different crystal planes (Table 3). The core level energies are shifted by about +1.5 eV for atoms in the top layer and +2.2 eV in the sub-surface layers compared to the atomic LDF one-particle Li 1s core level energy of $e_{1s}^{\text{atom}} = -51.11$ eV. These shifts – although they are not directly related to core level ionization energy shifts – agree with the general rationalization of core level shifts derived for simple metals [62–65]: the higher the coordination of an atom the lower the corresponding core level ionization energy. From HF calculations on large Li clusters it was concluded [62,63] that the core level binding energies are mainly determined by the initial state. Furthermore, also the total charge of the cluster has only very little influence on core level energies [62]. This conclusion was corroborated by experiments on Pt clusters.
adsorbed on teflon and SiO$_2$ [63]. Similar conclusions can be drawn from Kohn–Sham core level energies. In Li clusters embedded in extended Li(001) slabs, Li 1s core level energies are independent of the Mulliken charge of the individual atoms, but correlate with the coordination of the atom [24] as stated above. The same is true for the Li slab models of the present calculations where one finds (Table 3):

$$\varepsilon_{1s}^{\text{atom}} < \varepsilon_{1s}^{\text{surf}} < \varepsilon_{1s}^{\text{bulk}}.$$  \hspace{1cm} (4)

Because of the highly localized nature of the core level wave functions, an alternative rationalization may be offered for the core level shifts, relating them directly to the differences in the effective one-particle Hamiltonian at the different atomic sites. These differences are substantially determined by the dipole step of the Hartree potential, due to the charge redistribution near the Li(001) surface. The argument may be illustrated with the help of the simplified model of a homogeneous charge distribution parallel to the surface (Fig. 3). The top-layer Li atoms are localized on the increasing ramp of the induced Hartree potential, while all the sub-surface Li atoms are localized below the dipole barrier. To corroborate this picture quantitatively, at least to some degree, we have calculated the surface averaged induced charge density differences $\Delta \rho(z)$ and the resulting additional electrostatic potential

$$\Delta V_H(z) = -2\pi \int \frac{|z-z'|\Delta \rho(z')}{|z-z'|} \, dz'. \hspace{1cm} (5)$$

In a similar way the surface averaged crystal field $V_{\text{crys}}^{\text{super}}(z)$ of the superimposed atomic charge density is computed, which has been used as the reference density for the induced charge density difference $\Delta \rho(z)$. This simplified analysis results in repulsive changes $\Delta V_H$ of the induced Hartree potential, by $+2.3$ eV in the top surface layer and by $+3.5$ eV in all sub-surface layers. These changes always overcompensate the attractive crystal field contribution $V_{\text{crys}}^{\text{super}}$ of the superimposed Li atoms ($-0.8$ and $-1.5$ eV, respectively). Thus the shape of the potential curve displayed in Fig. 3 qualitatively represents the situation inside the Li(001) surface. The sum of the two contributions $V_{\text{crys}}^{\text{super}}$ and $\Delta V_H$ amounts to $+1.5$ eV for the surface layer and to $+2.0$ eV for all bulk Li atoms, in essentially quantitative agreement with the computed core level shifts from the slab models.

### 3.4. Quantum size effects

It has been known for some time that characteristic quantities of free electron gas model slabs exhibit an oscillatory behavior as a function of the slab thickness due to the boundary conditions on the wave functions [66,67]. Feibelman and Hamann have argued [68] that these effects should not be measurable in epitaxially grown thin films. Nevertheless, it seems worthwhile to investigate possible quantum size effects in thin metal films, especially in the context of slab convergence, similar to previous investigations on Al [44–46] and Li [29] films.

In contrast to examples for aluminium films, lithium films do not exhibit any significant

---

Fig. 3. Schematic view of the induced electron distribution (a) and the resulting Hartree potential (b) in the Li(001) surface, whose extent is symbolized by a rectangle in jellium-like fashion. The position of the lithium atoms are marked by the vertical ticks, with $j$ denoting the surface ($j=1$) and sub-surface crystal planes ($j>1$).
quantum size effect of the cohesive energy, neither in its high-temperature phase (Table 1, left-hand side) nor in its low-temperature phase (Table 1, right-hand side). The core level energies and the work function (negative Fermi energy) of the Li(001) model slabs, however, clearly exhibit some oscillations (Table 3). To investigate these oscillations in more detail, the Fermi level as well as the top-layer and sub-surface core level energies are plotted in Fig. 4 as a function of the number of atomic layers in the slab. Except for the step of 0.9 eV in the \( \epsilon_{1s}^{\text{surf}} \) curve between the mono- and the bi-layer (see the discussion above), the oscillations amount to \( \pm 0.2 \) eV and thus are significantly smaller than, for example, for Al(111) where variations of the work functions between 0.5 and 0.9 eV were found [44–46,68].

However, the most striking feature of the curves in Fig. 4 is that the oscillations in the core level energies run almost parallel to those of the Fermi level. Hence no quantum size effect on the core levels occurs inside the lithium slabs, the band structure as a whole is pinned at the weakly oscillating Fermi level. One should keep in mind that the work function is very sensitive to the charge distribution outside the surface. Thus even minor deviations in the vacuum charge distribution of the various Li(001) slabs, e.g. due to variations in the LCGTO representation of the wave function tails, may cause the observed oscillations in the work function, which in turn affect the core levels.

The average work function of the various multi-layer Li(001) slabs, however, amounts to 3.0 eV and is in good agreement with the experimental value of 2.9 eV [69].

4. The hydrogen adsorption at Li(001)

The most common adsorption sites of a bcc (001) surface are the four-fold hollow site, the two-fold bridge site between two neighboring surface atoms and the singly coordinated on-top site above one of the Li atoms. Due to the high tendency of hydrogen to diffuse into the Li bulk [1] and due to the general preference of single adatoms for highly coordinated adsorption sites, the on-top position is the most unlikely among these three. This is confirmed by theoretical studies. In model cluster calculations (based on free clusters [12–14,16] as well as on embedded clusters [19,25]) it was found that the binding energy for the on-top site is about 1.0 eV lower than for the hollow site. With increasing hydrogen coverage, this difference is lowered to 0.5–0.6 eV according to periodical HF model slab calculations [19]. The remaining two adsorption sites, however, are energetically very similar. Multi-reference CI cluster calculations [12,13] found hydrogen adsorbed at the bridge site about 0.2 eV (0.3 eV without correlation) more stable than at the hollow site. Similarly, in a recent DFT study on H/Li(001) model clusters embedded in a Li(001) monolayer [26] the bridge site was found to be more stable by about 1.2 to 1.3 eV, depending on the cluster size. CI many body perturbation theory calculations on cluster models [14,16] do not give a unique preference to any of the two adsorption sites. On the other hand, using the HF based EMBED formalism [27] for clusters embedded into Li(001) slabs of up to five layers, the hollow site was found to be significantly more stable by 0.3–0.9 eV [19]. This result seems to indicate that, at least at the HF level of theory, the hollow site is preferred over the bridge site when the lithium substrate is explicitly taken into account. Unfortunately, the accompanying HF slab model calculations for various hydrogen coverages were
only performed for adsorption at the on-top and the hollow site [19].

As can be seen from this brief review, the question of the preferred adsorption site for atomic hydrogen on Li(001), four-fold hollow or two-fold bridge, is still undecided. To facilitate the comparison with the recent periodic HF slab model investigation [19] as well as with our own MLEC-LDF cluster embedding study [25,26] we have focused on the four-fold hollow adsorption site. Hydrogen adsorption is assumed to take place in well-ordered overlayers. To model different adsorbate coverages (from \( \Theta = 1 \) ML, the monolayer, down to \( \Theta = 1/4 \) ML) the quadratic overlayers \( p(1 \times 1) \), \( c(2 \times 2) \) and \( p(2 \times 2) \) have been considered (Fig. 5), and the common “sandwich” geometry with adsorbates on both sides of the slabs has been adopted for computational efficiency. To examine the mutual interaction of the two separate adsorbate layers, the \( c(2 \times 2) \) “sandwich” structure is realized in two different ways. In the first geometry, referred to as \( c_m(2 \times 2) \), the hydrogen atoms in the two adsorbate layers are placed opposite to each other so that they are related by a mirror plane. In the second variant, denoted by \( c_g(2 \times 2) \), the “bottom” adsorbate layer is displaced by one lattice parameter along the [100] direction, resulting in a geometry with glide plane symmetry (Fig. 5). For sufficiently thick substrate slabs both geometries, \( c_m(2 \times 2) \) and \( c_g(2 \times 2) \), should lead to the same adsorption characteristics. The model for the \( p(2 \times 2) \) overlayer was constructed by displacing the bottom hydrogen layer with respect to the top layer by \( \sqrt{2}a \) along the [110] direction, to minimize the mutual interaction between hydrogen atoms in the two opposite adsorbate layers. This results in a structure which is more similar to the \( c_g(2 \times 2) \) model than to the simple \( c_m(2 \times 2) \) “sandwich”.

The interaction of simple metals with atomic hydrogen at low temperatures (<150 K) is quite different for the various metals [7]. While for metals with high valence charge density (e.g. Be and Al) the isolated atoms are simply chemisorbed without any significant charge transfer, hydrogen penetrates metals with low valence charge density (e.g. Na and K) by forming the corresponding metal hydride [7]. Lithium as a metal with intermediate valence charge density exhibits a behavior between these two extremes. Sprunger and Plummer deduced from the appearance of an additional peak in the x-ray photoemission spectrum and from the vanishing of the surface plasmon signal in the EELS spectrum that the adsorption of hydrogen on the lithium surface is accompanied by a strong charge transfer onto the adatom [7], resulting in the formation of a thin lithium hydride-like surface layer.

It is the main goal of the following discussion to corroborate this picture. We will proceed in three steps. The first part is devoted to the charge distribution and the bonding mechanism in H/Li(001) in general, while in the second part the adsorption characteristics and their dependence on the hydrogen coverage and on the slab thickness will be discussed in more detail. In the final part, the results of different techniques to quantify the charge separation within the surface LiH film will be compared to each other.

4.1. The adsorbate-substrate interaction in H/Li(001)

For a first qualitative insight into the adsorption mechanism, the hydrogen induced charge
rearrangement in the Li(001) surface is visualized in Fig. 6 for a seven-layer slab model of the p(1×1) structure. The charge density difference is taken between the H/Li(001) system at full monolayer coverage and its constituents, a clean seven-layer Li(001) slab and an isolated bi-layer of atomic hydrogen. As can be seen from this figure, hydrogen almost completely enters into the top crystal plane. This was to be expected from the experimental data [7]. The optimized adsorption height amounts to only 0.13 Å (see Table 5), a result which is in very good agreement with those of the embedded cluster DF study, 0.18–0.19 Å [25,26]. HF and CI calculations gave values between 0.00 and 0.26 Å [12–14,16,19]. The expected charge transfer to the more electronegative hydrogen is also clearly discernible. However, most striking is that the charge rearrangement occurs essentially parallel to the surface (see Fig. 6). Although closer to the adsorbate, the sub-surface Li atom directly underneath the adsorbate does not seem to be involved in the formation of the adsorbate-substrate bond. This unusual behavior is not restricted to the p(1×1) coverage. The charge density difference maps for the lower hydrogen coverage models exhibit quite similar structures, as do the results of the MLEC-DF cluster embedding study on single hydrogen adsorption at the four-fold site of the Li(001) surface [25]. Because of the different stoichiometry, Li2H and Li4H, of the c(2×2) and p(2×2) overlayers, the charge on the surface Li atoms around the adsorbed hydrogen is lower than in the case of full monolayer coverage. In corresponding density difference maps (not shown here) an additional trend toward a slightly less ionic hydrogen adsorbate is observed. For lower coverage values the lateral charge transfer becomes localized at the direct surface neighbor atoms of the adsorbate. In this case the amount of electronic charge density which is taken from the sub-surface three-center bonds rather than directly from the surface Li atoms (for a more detailed discussion of this distinction see Section 4.3) increases to some extent with lower hydrogen coverage. Qualitatively similar findings have also been obtained with the HF-EMBED cluster approach [19]. All this may be taken as a confirmation of the experimentally derived picture where the formation of a surface hydride has been deduced [7]. Due to this charge rearrangement within the p(1×1) H/Li(001) adsorption system, neither a significant induced surface dipole moment nor a significant change in the work function is expected for hydrogen adsorption on Li(001). Both expectations are confirmed by the results of the various H/Li(001) slab models which are summarized in Table 5. The mean value of the induced dipole moment and of the changes in the work function amount to just 0.09 Debye (1 Debye = 0.3934 au) and 0.14 eV, respectively.

Further evidence for the formation of a lithium hydride-like surface layer in the H/Li(001) adsorption systems can be deduced from the one-particle energy spectra of the slab models in combination with a population analysis of the corresponding crystal orbitals (Bloch waves). In Fig. 7 the band structure of the H/Li(001) adsorption system is compared to the band structures of the corresponding clean Li(001) slab and free H monolayer. For the sake of a transparent presentation a three-layer substrate slab and the p(1×1) overlay have been chosen for this figure. Qualitatively the same band structures were found for the other H/Li(001) slab models. The three partially filled valence bands of the clean Li(001) three-layer slab are clearly discernible (right panel). Due to the interaction with the 1s state of the free hydrogen monolayer (left panel), two of the Li valence bands are shifted
downward, forming a separate band complex around $-7$ eV (middle panel), while the remaining third Li valence band stays more or less unchanged (Fig. 7). To reveal the chemical character of the underlying crystal orbitals an overlap population analysis [70,71] of the valence bands has been carried out. The values given in Table 4 have to be regarded with due reservation because of the rich basis sets used in the present investigation.

### Table 4

Overlap population analysis of the valence bands of the three-layer H/Li(001) adsorption model at full monolayer p(1x1) coverage

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>&quot;LiH-like&quot; bands</th>
<th>&quot;Metallic&quot; bands</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>Li$_{surf}$</td>
</tr>
<tr>
<td>H</td>
<td>1.58</td>
<td>0.87</td>
</tr>
<tr>
<td>Li$_{surf}$</td>
<td>0.87</td>
<td>1.60</td>
</tr>
<tr>
<td>Li$_{sub}$</td>
<td>-0.12</td>
<td>-0.73</td>
</tr>
<tr>
<td>Total</td>
<td>2.33</td>
<td>1.74</td>
</tr>
</tbody>
</table>

The various populations are presented as reduced charge matrices whose diagonal elements are the net charges of each subsystem, while the off-diagonal elements represent the overlap populations. The Mulliken gross charges of the subsystems are given in the last row. The hydrogen orbitals (H), the surface Li orbitals (Li$_{surf}$) and the sub-surface Li orbitals (Li$_{sub}$) are used as subsystems. The valence bands are split into two different band complexes, according to the band structure displayed in Fig. 7, the low-lying “lithium hydride-like” bands and the “metallic” valence bands around the Fermi level. While the first of these band complexes is completely filled with four of the overall five valence electrons per unit cell, the latter complex carries a single electron per unit cell.

Anyhow, these populations will permit a qualitative distinction between bonding and anti-bonding contributions.

In agreement with the picture of an almost complete parallel charge transfer due to hydrogen adsorption at the Li(001) surface, the crystal orbitals belonging to the low-lying bonding band complex (denoted as “LiH-like” band in Table 4) are essentially restricted to the surface atoms, as can be deduced from the Mulliken population of the sub-surface Li atom (Li$_{sub}$) which amounts to only $-0.07$ au (out of 4.00 au). Furthermore, these crystal states exhibit a bonding character (positive overlap population) between the surface hydrogen and lithium atoms (H and Li$_{surf}$) and an anti-bonding character (negative overlap population) toward the sub-surface atoms. It is also remarkable that the H–Li$_{sub}$ overlap population with $-0.12$ au is significantly smaller than the other ones, confirming that the nearest-neighbor Li atom of the adsorbed hydrogen are much less involved in the formation of the Li–H bond than the lateral Li neighbors. On the other hand, the remaining valence states which are connected to the high-lying valence band around the Fermi level (Table 4, right-hand side) are almost purely metallic; the hydrogen population of these Bloch waves amounts to 0.07 au (out of 1.0 au). Analyzing the overlap populations one finds that there is a bonding Li–Li interaction in the metallic valence states, while the interaction towards the hydrogen atoms is weakly anti-bonding in this band.
In summary, it seems adequate to characterize the \( p(1 \times 1) \) H/Li(001) adsorption system as a LiH monolayer whose hydride anions are only weakly interacting (most probably by Pauli-repulsion) with the pure metallic states of the Li(001) support. This latter interpretation is suggested by the vertical H–Li distance, 1.88 Å, which is significantly shorter than the corresponding experimental value in crystalline lithium hydride, 2.04 Å [72]. The overall attractive interaction between the surface layer and the underlying sub-surface one is due to the bonding Li–Li interaction between these layers. The fact that the dispersion of the “LiH-like” band complex (2.74 eV, see Table 7) is comparable to the dispersion of the valence band of a free LiH monolayer expanded to the lattice constant of the Li support (running between −6.68 and −4.18 eV) can be regarded as a further corroboration for this picture. Finally it should be mentioned that Casassa and Pisani, too, found some indication for a more preferable charge transfer along the surface in the Mulliken charges derived from the HF densities of extended H/Li(001) slab models [19].

4.2. The adsorption system H/Li(001)

To characterize the hydrogen adsorption on the Li(001) surface the optimized adsorption height of hydrogen above the first crystal plane, the resulting binding energy per adsorbed hydrogen atom, and the vibrational frequency of the collective hydrogen stretching mode of all the slab models investigated are summarized in Table 5. Also given are the induced dipole moment per adsorbate, the adsorption-induced change of the work function and the charge transfer (Mulliken population) into the adsorbate. A first inspection of this table reveals that, although there are some significant deviations, the observables of the adsorption system H/Li(001) are in general rather unaffected by the geometrical changes of model systems. More explicitly, the mean variations of the characteristic quantities over the whole range of the different slab models employed amount to only \( \pm 0.03 \) Å for the adsorption height, to \( \pm 0.08 \) eV for the binding energy, to \( \pm 32 \) cm\(^{-1}\) for the vibrational frequency, and to \( \pm 0.04 \) au for the hydrogen charge. The deviations of the induced dipole moments and the changes in the work function seem to be more profound, but, as already mentioned above, these quantities are rather small. Nevertheless two interesting trends are discernible in the adsorption characteristics of the various H/Li(001) model slabs (Table 5).

The first point to be discussed concerns the slab convergence. The differences between the results of the seven-layer slabs and the five-layer slabs are much smaller than the corresponding differences between the three-layer and the five-layer model slabs. With deviations of 0.01 Å for the adsorption height, at most 0.05 eV (1 kcal/mol) for the binding energy, and about 0.03 au for the adsorbate charge, the results of the seven-layer model slabs are

<table>
<thead>
<tr>
<th>Quantity</th>
<th>( n )</th>
<th>( \Theta = 1 )</th>
<th>( \Theta = 1/2 )</th>
<th>( \Theta = 1/4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( h_a ) (Å)</td>
<td>3</td>
<td>0.08</td>
<td>0.14</td>
<td>0.19</td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>0.14</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.13</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>( E_b ) (eV)</td>
<td>3</td>
<td>2.91</td>
<td>2.74</td>
<td>2.97</td>
</tr>
<tr>
<td>5</td>
<td>2.94</td>
<td>2.85</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.99</td>
<td>2.84</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>( \omega_c ) (cm(^{-1}))</td>
<td>3</td>
<td>874</td>
<td>810</td>
<td>803</td>
</tr>
<tr>
<td>5</td>
<td>859</td>
<td>817</td>
<td>808</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>842</td>
<td>801</td>
<td>798</td>
<td></td>
</tr>
<tr>
<td>( q_H ) (au)</td>
<td>3</td>
<td>−0.20</td>
<td>−0.21</td>
<td>−0.20</td>
</tr>
<tr>
<td>5</td>
<td>−0.28</td>
<td>−0.25</td>
<td>−0.26</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>−0.31</td>
<td>−0.28</td>
<td>−0.28</td>
<td></td>
</tr>
<tr>
<td>( \Delta \mu_c ) (D)</td>
<td>3</td>
<td>−0.06</td>
<td>−0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>−0.03</td>
<td>0.13</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>0.18</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>( \Delta \Phi ) (eV)</td>
<td>3</td>
<td>0.05</td>
<td>−0.18</td>
<td>−0.13</td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>−0.22</td>
<td>−0.11</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>−0.09</td>
<td>−0.30</td>
<td>−0.33</td>
<td></td>
</tr>
</tbody>
</table>

The displayed quantities are: the height \( h_a \) of the hydrogen atom above the top Li(001) crystal plane, the binding energy \( E_b \) per hydrogen atom calculated via \( E_b = [\Theta^{-1}E_{\text{tot}}(\text{Li}(001)) + 2E_{\text{tot}}(\text{H}) - E_{\text{tot}}(\text{H/Li}(001))] / 2 \), the harmonic frequency \( \omega_c \) of the collective hydrogen mode perpendicular to the surface, the Mulliken charge \( q_H \) of the adsorbate, the induced dipole moment \( \mu_c \) per hydrogen atom \( \Delta \mu_c = \mu_c(\text{H/Li}(001)) - \Theta^{-1} \mu_c(\text{Li}(001)) \) in the upper half-space \( z \geq 0 \) of the symmetric H/Li(001) slab model, and the change in the work function \( \Delta \Phi \) induced by the adsorbate. For the difference between the \( c_m(2 \times 2) \) and \( c_p(2 \times 2) \) model see Fig. 5.
essentially stable to chemical accuracy. The calculated vibrational frequencies seem to be less stable, but one has to take into account that these values are determined by a finite difference method and a variation of 10–20 cm\(^{-1}\) is comparable to the error bars of this procedure. An exception from this general layer independence of the adsorption properties is provided by the induced dipole moment. These results clearly exhibit a trend to more positive values with increasing number of substrate layers, which consistently correlates with a corresponding trend to more negative changes of the work function (Table 5). As already pointed out in the MLEC-DF embedded cluster study [25], the positive values of the adsorbate-induced dipole moment of H/Li(001) are not related to the negative charge of the adatoms, but are determined by the polarization within the lithium substrate that accompanies the hydrogen adsorption. The same conclusion can be drawn from the present band structure calculations. Neither the Mulliken charge of the adsorbate nor the hydrogen charges derived by alternative methods to be discussed in the next section (see Table 8) are compatible with the observed values of the induced dipole moment. Instead, this effect has to be attributed to the polarization of the Li atoms directly underneath the adsorbate. As can easily be seen from the density difference map in Fig. 6, these lithium atoms are polarized toward the negatively charged adsorbate, which (according to the observed upward trend in the induced dipole moment) is obviously more easy to achieve in substrate slabs with more metal layers.

Second, the differences between the two variants \(c_m(2 \times 2)\) and \(c_g(2 \times 2)\) of the \((2 \times 2)\) overlayer structure (Fig. 5) are, as expected, still quite distinct for the three-layer slab models, but decrease significantly with increasing slab thickness (Table 5). For the seven-layer slab models the differences become either negligible, as for the vibrational frequency (3 cm\(^{-1}\)), for the induced dipole moment (0.04 D), and for the change of the work function (0.03 eV), or they even vanish completely, like those of the adsorption height and of the adsorbate charge. Only for the binding energy a small systematic deviation of about 0.05 eV seems to remain (Table 5). The possibility of a direct Coulomb interaction between the two ionic LiH-like surface layers may be checked by estimating the order of the non-homogeneous contributions of the electrostatic interaction of the two variants of the \((2 \times 2)\) structure (the homogeneous contribution is the same for both geometries) using a simple point charge model. Even if the nominal value of ± 1 au for perfect ionicity is used for the two point charge layers, the direct Coulomb interaction amounts to a difference of 10\(^{-6}\) au and thus is completely negligible. Because of the large distance of 10.47 au, a direct “through-space” interaction can also by excluded. Hence, an indirect, “through-bond” interaction involving Bloch waves inside the lithium substrate should be responsible for the calculated binding energy difference. The small, but non-vanishing polarization structures inside the H/Li(001) model slab which are discernible in the charge density difference map (Fig. 6) may be regarded as an indication for the existence of such an indirect interaction. Such an interaction may be seen more clearly in Fig. 8, where the shapes of the odd and the even lithium hydride-like crystal orbitals at the \(\Gamma\)-point are sketched along the \([001]\) direction, perpendicular to a seven-layer H/Li(001) model slab. Except for their different signs, these two wave functions are practically identical near the surfaces. Although the one-particle energies of these states are located about 1 eV below the bottom of the valence bands of the clean Li(001) surface, they decay so slowly toward the interior of the metal substrate that even for a seven-layer substrate slab they still exhibit some admixtures of a central layer Li atom orbital, depending on the symmetry of the wave functions. This effect is expected to be differently pronounced in the two structures \(c_m(2 \times 2)\) and \(c_g(2 \times 2)\).

Nevertheless the trends and differences just discussed are only minor effects, and we would like to emphasize once more that in general the adsorption properties are remarkably independent of slab thickness and of hydrogen coverage. In Table 6 these data are compared to the predictions from other calculations on the H/Li(001) adsorption system. A comparison with the results from a MLEC-DF cluster embedding study [25,26] is of major interest because this approach, like the present band structure calculation, is based on
Fig. 8. Sketch of the even (solid line) and odd (dashed line) “lithium hydride-like” crystal states at the Γ point of a $c_m(2 \times 2)$ model slab ($\Theta = 1/2$ ML) with seven substrate layers shown along the [001]-axis through the adsorbed hydrogen atoms. The position of the $j$th crystal planes is indicated by the vertical ticks labeled Li($j$).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>MLEC</th>
<th>FILMS$^a$</th>
<th>CRYS.TAL$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_B$ (Å)</td>
<td>0.18</td>
<td>0.13</td>
<td>0.26</td>
</tr>
<tr>
<td>$E_B$ (eV)</td>
<td>2.48</td>
<td>2.99</td>
<td>2.72</td>
</tr>
<tr>
<td>$\omega_s$ (cm$^{-1}$)</td>
<td>800</td>
<td>842</td>
<td>798</td>
</tr>
<tr>
<td>$q_H$ (au)</td>
<td>-0.12</td>
<td>-0.31</td>
<td>-0.50</td>
</tr>
<tr>
<td>$\Delta\mu_s$ (D)</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$^a$ Values obtained from a slab model with seven substrate layers. $^b$ Values obtained from a slab model with five substrate layers. See Table 5 for the definition of the various quantities. The results entitled MLEC are from the embedding study based on density functional theory [25], those entitled CRYS.TAL are from a periodic Hartree–Fock study [19]. The results of the present (FILMS) work are given in the two middle columns.

DFT, and employs the same XC potential approximation as well as identical GTO orbital basis sets. Taking into account the methodological differences of the two procedures, embedded clusters vs. extended slab model, the agreement of the observables is quite satisfactory. The difference in the optimized adsorption height, for example, amounts to only 0.04 Å. However, the binding energies obtained by the embedded cluster study are 0.5–0.6 eV lower than those calculated for the H/Li(001) slab models and similarly the values for the vibrational frequency are about 40 cm$^{-1}$ too low (Table 6). These observed differences are most likely due to the different hydrogen coverage. Although the calculated adsorption data of the H/Li(001) slab models do not exhibit any significant dependence on the hydrogen coverage, it cannot be ruled out that the results will differ somewhat in the limit of vanishing coverage which is not easily accessible with slab models. The present results agree reasonably well with those of a recent periodic HF slab model study [19]; this comparison is based on the largest substrate, both in simple “sandwich” geometry, of each investigation. The HF binding energies amount to 2.6–2.7 eV and thus are just 0.3 eV lower than the DF results of the present study. However, the HF adsorption height is found 0.13–0.38 Å larger than those of the present DFT calculation.

A simple measure to estimate the mutual interaction of atoms adsorbed on the two opposite sides of a model slab is provided by the splitting of the adsorbate induced energy bands which, in the present case, are related to the even and odd linear combination of the lithium hydride-like surface states (see Fig. 7). Analogously, the size of the
lateral interaction of adatoms can be measured by means of the dispersion of the adsorbate induced energy bands. The corresponding data for the various H/Li(001) model systems of the present study are summarized in Table 7. Despite a slight trend toward smaller values, the dispersion of the lithium hydride-like bands, defined as $\max_{k \in BZ} |E(k)| - \min_{k \in BZ} |E(k)|$, is essentially independent of the number of substrate layers of the slab model. As expected, the dispersion decreases with decreasing hydrogen coverage, from 2.74 eV for $\Theta = 1$ ML down to 0.29 eV for $\Theta = 1/4$ ML. The latter value is still remarkably high considering the fact that in the p(2×2) overlayer the lateral H–H distance amounts to 6.98 Å. It is a consequence of the adsorbate-substrate interaction within the LiH-like surface layers. Even in the already quite open p(2×2) overlayer, the four lateral nearest-neighbors of each adsorbed hydrogen atom are still in direct contact with each other. At least c(4×4) or p(3×3) overlayer structures with coverages of 1/8 to 1/9 ML would be necessary to separate the individual adsorption complexes reasonably well.

For the three-layer slab models the vertical interaction of the two lithium hydride surface layers results in a band splitting of about 0.5 eV (defined as $\max_{k \in BZ} |E_{even}(k)| - |E_{odd}(k)|$). The size of this splitting reveals that the three-layer slab models are not yet sufficiently thick to separate the two adsorbate layers, despite the fact that the interaction is mainly parallel to the surface. This is not surprising if one takes into account the shape of the involved wave functions (see Fig. 8). However, in agreement with the bonding mechanism the band splitting of 0.53 eV found for the three-layer p(1×1) slab model is significantly smaller than the dispersion of the corresponding bands, 2.74 eV, although in this model system the lateral H–H separation is exactly the same as the vertical one. With increasing number of substrate layers, the band splitting decreases considerably, to less than 0.10 eV for the five-layer slab and to $\leq 0.02$ eV for the seven-layer slab. Thus, at least for the seven-layer slab models, the two hydrogen layers may be regarded as essentially uncoupled. In this sense, slab convergence has been reached in the present study of the H/Li(001) adsorption system.

4.3. Charge separation in the H/Li(001) surface

The central aspect of high coverage atomic hydrogen adsorption at the four-fold hollow sites of a Li(001) surface is the formation of a lithium hydride-like surface monolayer, supported by an almost unchanged metallic substrate. In addition to the various indications discussed above, this interaction mechanism can also be seen from the total electron charge density of the H/Li(001)

| Table 7 |
|---|---|---|---|---|
| Dispersion $E_{T} - E_{M}$ and band splitting $\max_{k \in BZ} |E_{even}(k)| - |E_{odd}(k)|$ (see Fig. 7) of the “lithium hydride-like” bands of the H/Li(001) adsorption models (with hydrogen adsorbed at both sides of the substrate) as a function of slab thickness (number n of Li layers) and coverage $\Theta$ (in ML) |
| Quantity | n | $\Theta = 1$ | $\Theta = 1/2$ | $\Theta = 1/4$ |
| | | p(1×1) | c$_m$(2×2) | c$_g$(2×2) | p(2×2) |
| Dispersion (eV) | | | | | |
| 3 | 2.74 | 0.66 | 0.77 | 0.29 |
| 5 | 2.51 | 0.58 | 0.61 | |
| 7 | 2.50 | 0.58 | 0.56 | |
| LiH* | 2.50 | | | |
| Band splitting (eV) | | | | | |
| 3 | 0.53 | 0.54 | 0.58 | 0.35 |
| 5 | 0.04 | 0.09 | 0.10 | |
| 7 | 0.02 | 0.02 | 0.02 | |

* LiH monolayer expanded to the lattice constant of Li(001).

For the difference between the c$_m$(2×2) and c$_g$(2×2) model see Fig. 5.
adsorption system. As an example, the electron density of a seven-layer slab model at full monolayer hydrogen coverage, $p(1 \times 1)$, is shown in Fig. 9. The topological atom analysis [33,34] already applied to the clean Li(001) surface (Fig. 1) has also been carried out for the H/Li(001) slab models. While the non-nuclear attractors inside the substrate essentially remain, these regions are replaced in the surface layer by the topological hydrogen atoms. The structures discernible near the surface rather strongly resemble those found in a recent DF slab model study of the ionic MgO(001) surface [30,35]. The hydrogen atoms are, not unexpected for an ionic LiH layer, much larger than the topological surface lithium atoms, providing further evidence for the profound charge transfer along the (001) surface. According to the Mulliken populations (Table 5) this charge separation amounts to 0.2–0.3 au, in qualitative agreement with the results of the MLEC-DF cluster embedding study on the adsorption of single hydrogen atoms at the Li(001) surface [24–26]. The Mulliken charges found in the recent periodic HF slab investigation of H/Li(001) [19] are about twice as large (see Table 6). However, due to the differences in the orbital basis sets (a much more compact basis set has been employed for the HF study), the obtained Mulliken charges should not be directly compared.

Because of the well-known ambiguities of a Mulliken population analysis, we prefer to follow the strategy of a recent study on the charge separation in MgO(001) [30,35] and quantify the charge separation in the surface layer exclusively on the basis of well-defined physical quantities, like the charge density and the electrostatic potential. Since the details of the underlying methods have been described elsewhere [30], only a brief summary will be given here. The first method to determine effective charges for surface atoms is based on a Fourier analysis of the surface Madelung field

$$\phi(s, z) = \frac{2\pi}{A} \left( \sum_{K \neq 0} \frac{M_K}{|K|} e^{iKs} e^{-|K|z} + P_{\text{tot}} - Q_{\text{tot}} e^{-iKs} e^{-|K|z} \right)$$

above a two-dimensional periodic slab system. This strategy is particular useful for systems like H/Li(001) which do not exhibit a net total charge $Q_{\text{tot}}$ nor a total dipole moment $P_{\text{tot}}$ perpendicular to the surface. $K$ denotes the reciprocal lattice vectors, $A$ is the area of the surface unit cell UC, and $s$ and $z$ characterize the positions where the potential is to be evaluated: $z$ is the component normal to the surface and $s$ is the 2D projection onto the surface plane. An effective charge is then determined by matching the first non-vanishing coefficients $M_K$ in this expansion by those of a corresponding point charge array. Due to the damping factor $e^{iKs}$ in

$$M_K = \int_{-\infty}^{\infty} \int_{\text{UC}} \rho(s, z) e^{-iKs} e^{-|K|z} d^2s \, dz,$$

this analysis is highly surface sensitive. The second method to quantify the charge separation relies on the basis set independent subdivision of space according to the topological atom concept [33,34].

Both methods of quantifying the charge separation have been applied to the H/Li(001) model slabs which exhibit a closed packed $p(1 \times 1)$ overlay layer (Table 8). Like most of the adsorption properties of the H/Li(001) system, the resulting atomic
Table 8
Comparison of the charge separation (in au) in the top surface layer of the H/Li(001) adsorption system at full p(1×1) hydrogen coverage quantified by the three methods: a Mulliken population analysis of the induced charge separation, a direct analysis of the Madelung field above the surface and the integration of the charge density inside the topological atoms

<table>
<thead>
<tr>
<th>Layers</th>
<th>Mulliken population</th>
<th>Madelung field</th>
<th>Topological atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li</td>
<td>H</td>
<td>Li</td>
</tr>
<tr>
<td>3</td>
<td>+0.09</td>
<td>−0.20</td>
<td>+0.71</td>
</tr>
<tr>
<td>5</td>
<td>+0.25</td>
<td>−0.28</td>
<td>+0.76</td>
</tr>
<tr>
<td>7</td>
<td>+0.26</td>
<td>−0.30</td>
<td>+0.77</td>
</tr>
<tr>
<td>LiH*</td>
<td>+0.32</td>
<td>−0.32</td>
<td>+0.82</td>
</tr>
</tbody>
</table>

*LiH monolayer expanded to the lattice constant of Li(001).

charges, are practically independent of the number of substrate layers in the slab models. Only a weak upward trend of the charge separation with increasing number of substrate layers is discernible in the Mulliken populations and in the effective charges deduced from the Madelung field analysis. The total charge of the topological atoms are completely unaffected by the thickness of the slab (Table 8). However, it is most interesting to note that both, the Madelung field analysis as well as the topological atom approach, lead to a charge separation much larger than indicated by the Mulliken populations. While the effective Madelung charges amount to almost ±0.8 au, the charge separation determined by means of the topological atoms yields values close to ±1.0 au, the nominal value of perfect ionicity. A slightly reduced topological charge is found on the Li cations whenever its value is not forced to be equal to the anionic charge by symmetry as in the case of the LiH monolayer. Of course, equal charges are determined for the cations and the anions in the present Madelung field analysis because of the underlying assumption of a uniquely lateral charge transfer. The electronic charge of the hydrogen atoms originates to some extent (Mulliken populations: −0.03 to −0.11 au; topological atoms analysis: −0.13 au) from the sub-surface substrate layer. This effect may be connected to the regions of negative charge around the surface anions which, as indicated in the charge density difference map (Fig. 6), extend into the three-center bonds between the first and second crystal layer. An estimated 10–20% of the hydrogen charge is directly taken from the three-center bonds underneath the surface. In summary, a lateral charge transfer of about 0.75 au (Madelung field analysis) or of about 0.9 au (topological atom approach) is found. Even though the two charge density based methods yield somewhat different results (for an explanation see Ref. [30]), it is obvious that the Mulliken populations, 0.2–0.3 au, strongly underestimate the lateral charge separation in the H/Li(001) adsorption system.

Finally it should be mentioned that each of the three methods employed to quantify the charge separation in the p(1×1) H/Li(001) surface layer yields essentially the same results when applied to a free LiH monolayer expanded to the lattice constant of the metallic support (see Table 8); the deviations amount to 0.02–0.09 au. Hence, at least concerning the charge separation, the lithium hydride-like surface layer in H/Li(001) is almost unaffected by the lithium substrate, indicating a rather weak interaction between the ionic surface layer and its underlying metallic support (see also discussion in Section 4.1).

5. Summary and conclusions

Lithium, although an alkaline metal, exhibits some rather atypical features for a metal. Like beryllium and boron, it tends to form multi-center bonds. This characteristic property of lithium is not only recognizable in its special chemical reactivity, but is also directly discernible at the quantum chemical level as local extra-atomic
maxima in the electron density. Because of these three-center bonds lithium, to some extent, is more similar to a covalent solid than to a typical s electron metal. No long-range charge density oscillations are found near the surface of crystalline lithium. Instead a profound charge accumulation between the surface and the first sub-surface layer occurs, followed by an almost unchanged lithium crystal underneath. For all the quantities investigated, the onset of typical bulk-behavior was observed as soon as one sub-surface layer was present in the Li(001) slab models. Moreover, due to the special charge distribution inside the (001) surface, lithium, in contrast to other jellium-like metals, exhibits a positive surface dipole moment pointing out of the (001) surface. Furthermore, no significant quantum size effects could be found within thin Li(001) films.

The adsorption of atomic hydrogen in the fourfold hollow site at full monolayer coverage is characterized by the formation of a LiH-like surface monolayer, theoretically corroborating the findings of recently published EELS and XPS experiments on the hydrogen adsorption at the bcc(001) surface of lithium \cite{7}. Adsorbed hydrogen atoms almost completely enter into the first Li(001) crystal plane, and a strongly ionic surface layer is formed. The charge separation within the surface layer was quantified using two independent methods, both uniquely based on the well-defined charge density of the H/Li(001) adsorption system. The charge separation within the surface layer amounts to almost ±1 au, the nominal value for perfect ionicity in LiH. At full monolayer coverage (p(1 × 1) overlayer) as well as for the lower coverages investigated (c(2 × 2) and p(2 × 2) overlayers) the adsorption-induced charge transfer essentially occurs within the surface layer. Although closest to the adsorbate, the Li atom directly underneath the four-fold hollow site is not significantly involved in the formation of the Li–H bond. Only a weak anti-bonding interaction between the adsorbate and the lithium atoms of the second crystal plane is discernible. The lithium substrate supporting the LiH-like surface monolayer stays metallic. Thus it seems more appropriate, at least at full monolayer coverage, to characterize the adsorption system H/Li as an insulator–metal interface than as a typical chemisorption system at a metal surface. The bonding interaction at this interface is mainly due to the formation of three-center bonds between the lithium atoms on both sides of the interface.

The observables of the hydrogen adsorption on Li(001) do not exhibit any significant dependence on the number of atomic layers in the slab models employed nor on the hydrogen coverage modeled by the overlayers of different densities. Yet, because of the strong lateral orientation of the H–Li interaction, the p(2 × 2) overlayer is not sufficiently sparse to simulate single hydrogen adsorption. On the other hand, according to our results, model convergence is essentially reached with H/Li(001) slabs of seven lithium substrate layers.

Acknowledgements

We thank O.D. Häberlen and S. Krüger for stimulating discussions, and S. Casassa and C. Pisani for providing us with the results of their HF study on H/Li(001) prior to publication. The work of N.R. was supported by the Deutsche Forschungsgemeinschaft via SFB 338 and by the Fonds der Chemischen Industrie; the work of J.C.B. was supported by the United States Department of Energy.

References