Effect of the cluster size in modeling the H\textsubscript{2} desorption and dissociative adsorption on Si(001)

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Three different clusters, Si\textsubscript{8}H\textsubscript{12}, Si\textsubscript{15}H\textsubscript{10}, and Si\textsubscript{21}H\textsubscript{20}, are used in density-functional theory calculations in conjunction with \textit{ab initio} pseudo potentials to study how the energetics of H\textsubscript{2} dissociative adsorption on and associative desorption from Si(001) depends on the cluster size. The results are compared to five-layer slab calculations using the same pseudopotentials and high quality plane-wave basis set. Several exchange-correlation functionals are employed. Our analysis suggests that the smaller clusters generally overestimate the activation barriers and reaction energy. The Si\textsubscript{21}H\textsubscript{20} cluster, however, is found to predict reaction energetics, with \(E_{\text{a}}^{\text{des}} = 56 \pm 3\) kcal/mol (2.4 \pm 0.1 eV), reasonably close (though still different) to that obtained from the slab calculations. Differences in the calculated activation energies are discussed in relation to the efficiency of clusters to describe the properties of the clean Si(001)-2\times1 surface.

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I. INTRODUCTION

Cluster models are a frequently used tool for studying different aspects of physics and chemistry of clean surfaces, adsorption, and surface chemical reactions. An example which attracted considerable experimental and theoretical interest over the last years is the H dissociative adsorption and associative desorption on the Si(001)-2\times1 surface \[\text{H}_{2}\text{Si(001)}\] which is a subject of this study. The intriguing experimental result that the H desorption from Si(001) follows first-order kinetics \[\text{H}_{2}\text{Si(001)}\] has triggered an intense theoretical activity in this field mainly concentrated on the mechanism(s) leading to such an unusual behavior.

The available first principles calculations address the latter question on the basis of two different models: (i) the cluster approximation using either configuration-interaction (CI) methods \[\text{H}_{2}\text{Si(001)}\] or density-functional theory (DFT) \[\text{H}_{2}\text{Si(001)}\] to describe the exchange and correlation effects or (ii) extended slab models for the Si(001)-2\times1 surface using DFT calculations.

The DFT slab calculations all agree in their conclusions supporting the \textit{pre-pairing} mechanism \[\text{H}_{2}\text{Si(001)}\] according to which two hydrogens are pre-paired on the same Si surface dimer and associatively desorb through an asymmetric transition state (TS). The cluster calculations, however, have led to different conclusions. All these calculations find a rather high barrier for desorption of two hydrogens from a single Si dimer, e.g. \(E_{\text{a}}^{\text{des}} = 74-75\) kcal/mol (3.2 eV) \[\text{H}_{2}\text{Si(001)}\], 85-86 kcal/mol (3.7 eV) \[\text{H}_{2}\text{Si(001)}\], 82-85 kcal/mol (3.6-3.7 eV) \[\text{H}_{2}\text{Si(001)}\]. Comparing to the experimental activation energy of desorption of \(\sim 58\) kcal/mol (2.5 eV) \[\text{H}_{2}\text{Si(001)}\], these findings were interpreted as being compelling evidence against the pre-pairing mechanism. In an attempt to reconcile the experimentally observed energetics and kinetics of desorption from the monohydride phase, various defect-mediated mechanisms \[\text{H}_{2}\text{Si(001)}\] were suggested including formation of metastable dihydride species as an intermediate step. All the above studies have in common that their argumentation rests on computational schemes based on CI and the small and simple Si\textsubscript{8}H\textsubscript{12} cluster to model the Si(001)-2\times1 surface except the work by Nachtigall \textit{et al.} \[\text{H}_{2}\text{Si(001)}\] where DFT has been employed. In some studies larger clusters, like Si\textsubscript{15}H\textsubscript{10} or Si\textsubscript{21}H\textsubscript{20} have been used. Nevertheless, the effect of cluster size on the energetics of H\textsubscript{2} adsorption/desorption on Si(001) has not been analyzed in detail in the literature.

The only cluster-based support to direct desorption via the pre-pairing mechanism comes from the DFT calculations by Pai and Dorez \[\text{H}_{2}\text{Si(001)}\]. Using the non-local Becke-Lee-Yang-Parr (BLYP) functional \[\text{H}_{2}\text{Si(001)}\], they find \(E_{\text{a}}^{\text{des}} = 64.9\) kcal/mol (2.8 eV) including a zero-point energy (ZPE) correction. Given the uncertainties originating both from the use of different functionals and from inherent limitations of the cluster approximation, they considered their result to be compatible with the experimental desorption energy. The first possible source of error, the reliability of the functional, was addressed by Nachtigall \textit{et al.} \[\text{H}_{2}\text{Si(001)}\], who systematically compared various density functionals to the results of the state-of-the-art computational tool in quantum chemistry, an extrapolated quadratic CI method. For the sake of computational feasibility, they concentrated on a few simple test cases, four reactions involving silanes, and a Si\textsubscript{2}H\textsubscript{4} cluster with a geometry chosen to mimic H\textsubscript{2} desorption from Si(001). While the extrapolated quadratic CI method gives a reference value of 90.4 kcal/mol (3.92 eV) for \(E_{\text{a}}^{\text{des}}\) the Perdew-Wang (PW91) functional \[\text{H}_{2}\text{Si(001)}\] underestimates \(E_{\text{a}}^{\text{des}}\) by 9.5 kcal/mol (0.41 eV) compared to this reference. The Becke-Perdew (BP) functional \[\text{H}_{2}\text{Si(001)}\] gives an even lower barrier, \(E_{\text{a}}^{\text{des}} = 79.4\) kcal/mol (3.44 eV). Generally, Nachtigall \textit{et al.} find the B3LYP functional \[\text{H}_{2}\text{Si(001)}\] to give closest agreement with their CI calculations, while the BLYP functional is performing second best. A similar trend concerning the performance of different functionals was also observed in the case of H diffusion on the
Si(001)-2\times1 surface. However, we find it not to be a priori clear whether their conclusions could be applied to better cluster approximations to the Si(001) surface, because the electronic wave functions at a surface are generally more extended than in a cluster and this may naturally affect the electron-electron correlations. It is one of the aims of the present paper to study the performance of different functionals with the size of the clusters.

A second issue which hampers a clear-cut comparison of different approaches lies in the geometric structure of the clean Si(001) surface. While the DFT calculations give the correct description of the geometry of the clean Si(001) surface. While the DFT calculations of different approaches lies in the geometric structure of the clusters. This could imply substantial differences between the two approaches in the surface relaxation during the adsorption/desorption process as well as in the surface electronic structure. Since H2 dissociation on Si(001) is known to couple to the surface motion, one could expect these differences in the description of the clean Si(001) surface also to influence the reaction energetics predicted by different calculational approaches.

In the light of the above we find of particular interest to bridge the DFT slab and cluster calculations by studying the convergence of the H2 adsorption/desorption energetics with cluster size. Since the results of the DFT calculations agree about a direct desorption process and the very recent experiment by Flowers et al. also supports this mechanism, we shall perform our analysis adopting the pre-pairing scenario for the Si(001) surface. A description of the computational method used in the present work is given in the next section. In Sec. II particular attention is paid to the structure of the clean Si(001) surface. Clusters with one, two and three surface dimers are used in Sec. III to study the energetics of the adsorption/desorption process. A summary of the results and discussion is presented in the last section.

II. CALCULATIONS

A. The systems used for modeling H2/Si(001)

Generally, cluster models for surface chemical processes are treated in conjunction with a basis set for the electronic states consisting of localized orbitals. However, special care is required in choosing a basis set which meets the desired level of accuracy. In order to isolate the different approximations inherent in the choice of the cluster and the basis set size, we decide to perform total energy calculations within the DFT scheme as implemented in the fhimd package, employing a plane waves basis set with well-controlled convergence properties. We report results for the three different clusters shown in Fig. 1 (a), Si9H12, Si15H16 and Si21H20. Each of them represents the topmost four layers of the reconstructed surface. They differ by the number of Si-Si surface dimers they contain. The larger Si15H16 and Si21H20 clusters are derived from Si9H12 by adding one and two dimers, respectively, in the [110] direction along with their full coordination of second layer Si atoms, one third and one fourth layer Si atom. All dangling bonds of the silicons in the subsurface layers are saturated with hydrogen atoms. By increasing the cluster size in this way we aim at reaching three ascendingly improved approximations to the clean Si(001) surface: Si9H12 is the minimal one to represent the symmetric 2\times1 reconstruction; Si15H16 is the smallest cluster that enables to model the p(2\times2) surface reconstruction. Finally, Si21H20 contains one surface dimer surrounded by two others, thus having the same local environment as on the surface. In the context of H2 desorption from the monohydride phase, the larger clusters also allow to study the interaction between adjacent occupied dimers.

Since the super cell approach implemented in fhimd implies periodic boundary conditions for the wave functions, the clusters are placed in a sufficiently large orthorhombic unit cell, where they are separated by \approx 7 Å to avoid unwanted interactions. Since the electronic states of the cluster Hamiltonian have no dispersion, it is sufficient to calculate them at a single point in the Brillouin zone (BZ), k_c = (0,0,0).

To link the current discussion with the available slab calculations, we perform as a final step a set of calculations employing a p(2\times2) slab with five Si layers, Fig. 1 (b), similar to Ref. 13. The k-space integration is performed using 16 k\_f points in the whole surface Brillouin zone of the 2\times2 unit cell.
Both cluster and slab calculations are carried out using the local-density approximation (LDA) to the exchange-correlation functional, as obtained form the Monte Carlo results by Ceperley and Alder[1] in the parameterization of Perdew and Zunger.[2] For comparison all calculations are repeated with gradient corrections as described by the BP, PW91 and BLYP functionals. Our choice to include these functionals in the test is partially motivated by the shortcomings of the BP and PW91 functionals, cf. Ref. [11], found in the case of small systems. DFT plane-wave calculations employing either slabs or Si$_32$ or larger clusters and the BLYP functional have not yet been reported for the H$_2$/Si(001) reaction energetics.

We employ norm-conserving sp-nonlocal pseudopotentials for Si atoms, generated from a separate all-electron calculation of the Si atom for each exchange-correlation functional according to Hamann’s scheme[3]. For gradient-corrected DFT calculations, the use of these consistently constructed pseudopotentials ensures the proper description of core-valence exchange in each of the gradient-corrected functionals used.[4] For the hydrogens passivating Si dangling bonds, a s-nonlocal pseudopotential is generated following the Troullier and Martins prescription.[5] However, for the hydrogen atoms taking part in the reaction, we employ the full 1/r potential. For all energies quoted in the paper, plane waves with a kinetic energy up to $E_{\text{cut}} = 30$ Ry (408 eV) were included in the basis set. While geometries and relative energies for systems consisting entirely of Si atoms are well converged already at 18 Ry (245 eV), the high-quality basis set is required for a correct description of the hydrogen wave functions close to the core.

B. Structure optimization

We perform separate structure optimizations for each cluster size and for the LDA, BP, PW91 and BLYP functionals. The first step in all structure relaxation runs was to optimize the positions of the terminating hydrogens, with the subsurface silicon coordinates kept fixed at their bulk values, and the symmetric dimer bond length set to $d = 2.28$ Å as found in Ref. [10].

One of our present goals is to investigate to what extent clusters are appropriate for a description of the Si(001) surface. One important feature of the clean surface is the buckling of the Si surface dimers (see the next Section). It is therefore interesting to test if the buckling can be modeled by clusters of appropriate size. The failure of small clusters to reproduce the buckled surface structure is sometimes attributed to the neglect or underestimate of elastic interactions between Si dimers in this approach. However, the importance of elastic interactions is established only for the alternation of buckling angle (‘antiferromagnetic ordering’) in the $p(2 \times 2)$ or $c(4 \times 2)$ reconstruction[6]. To distinguish elastic from electronic effects, we employ a two-step procedure to determine the equilibrium structures of the bare clusters. First we sample the total energy as a function of the dimer buckling angle $\alpha$, as done, for example, in Refs. [16, 20], but without relaxation of any of the deeper layers. Thus any elastic interactions between Si dimers are avoided. Neighboring dimers (if there are any) are buckled in opposite directions, with buckling angles $\alpha$ and $-\alpha$, to mimic the $p(2 \times 2)$ surface reconstruction.

The structure of the bare clusters is finally determined by unconstrained relaxation of the topmost two Si layers. Here we use the energy minimum as a function of $\alpha$ determined in the previous calculations as input for the starting geometry. The two pairs of hydrogens saturating the second layer Si bonds in the [110] direction, which would correspond to adjacent Si dimers on the Si(001) surface, are also allowed to relax. We have also tested full relaxation of all layers in the case of the Si$_9$H$_{12}$ and Si$_{15}$H$_{18}$ clusters within LDA. The lack of any geometric constraints, however, tends to overestimate the surface relaxation and introduces unrealistic atomic displacements. Full relaxation would only be appropriate for clusters studied as objects in their own interest, rather than as an approximation to the Si(001) surface.

The structure of the monohydride phase is determined by relaxing the adsorbate and the two Si layers beneath it. In the case of the Si$_{23}$ cluster the H$_2$ molecule is adsorbed on the middle dimer. The geometries of transition states (TS) are determined by a search algorithm using the ridge method proposed by Ionova and Carter[38]. Since geometries are less sensitive to the quality of the basis set than the total energies, we have found it sufficient to perform geometry optimizations at a plane-wave cut-off of $E_{\text{cut}} = 18$ Ry. The structures are considered converged when all forces are smaller than 0.05 eV/Å.

III. THE CLEAN Si(001)-2×1 SURFACE

On the Si(001) surface, the surface Si atoms form dimers, leading to the (symmetric) 2 $\times$ 1 reconstruction. The surface can reduce its symmetry if the Si surface atoms relax to different heights, i.e. the dimers are buckled. This leads to the formation of lower symmetry patterns, the asymmetric $p(2 \times 1)$, $p(2 \times 2)$, $c(4 \times 2)$. These reconstructions are characterized by the dimer buckling angle $\alpha$, the dimer bond length $d$, and the energy favor per dimer $\Delta E$ with respect to the symmetric 2 $\times$ 1 reconstruction.

The calculations for H$_2$ desorption from Si(001) using slabs together with DFT and those based on many-body wave functions (like CI) already differ in their description of the clean surface geometry. In the latter calculations, mostly the Si$_9$H$_{12}$ cluster with one symmetric Si dimer was used as reference state for the clean Si(001) surface. Radeke and Carter verified that the symmetric cluster is
the geometric ground state at the level of theory used in their work. Recent theoretical studies on Si clusters come to conflicting conclusions and thus leave the discussion about the ground state symmetry of Si clusters still open.

On the other hand, the DFT slab calculations are consistent in their predictions and show good agreement with recent experiments. Direct evidence for the buckling comes from low-temperature STM images and structure determinations by LEED. Furthermore, observed core-level shifts are inconsistent with symmetric surface dimers, but can be explained by buckled dimers. The buckled surface reconstruction has gained further support by the good agreement between the measured dispersion of surface band states with calculations using the GW approximation.

The different symmetries of reconstruction correspond to different electronic structures at the surface. Previous theoretical work has established the following picture: After dimerization of the surface Si atoms, they would both remain to have dangling bonds occupied by one electron, i.e. a degenerate electronic ground state. There are two principal possibilities for a lowering of the electronic energy. Firstly, a bonding and antibonding linear combination of orbitals could be formed (similar to a π-bond in a free dimer), only one of which is occupied. In this case the Si surface dimer would remain symmetric. The second possibility is a Jahn-Teller-like splitting of the degeneracy. By buckling the Si dimer, the lower Si atom comes to an almost planar bonding configuration with its three neighbors, while the upper Si atom reaches a pyramidal configuration. A rehybridization of the orbitals at each of the Si atoms results in a lowering of the dangling orbital at the upper Si atom, and in an up-shift of the orbital at the lower Si atom, which is accompanied by a transfer of electron density from the lower to the upper atom. The preferred way of stabilization depends on several factors: the possible strength of the π-bond, the possible energy gain due to rehybridization, the ability of the system to screen the increased Coulomb repulsion in the dangling bond of the upper Si atom, and the energetic cost of elastic deformation in the deeper layers induced by the buckling. The ground state geometry is thus determined by an interplay of both elastic and electronic effects and could be quite sensitive to different surface reconstructions and computational methods.

Before we describe our own results for the ground state of clusters, we briefly discuss the recent literature. Yang et al. do not find buckling for the SiH12 cluster, either within Hartree-Fock or in a DFT calculation employing the B3LYP functional. Increasing the cluster size to Si15H16, however, unambiguously shows an energy favor for the buckled p(2 × 2) reconstruction, ~3–5 kcal/mol (0.15–0.23 eV) per dimer depending on the basis set used. Konečný and Dorel have used the same cluster and the BLYP functional to study H2O adsorption on Si(001)-2×1 and found a buckled dimer structure for SiH12 with α = 9.6°, ΔE = 0.05 kcal/mol (0.002 eV) and d = 2.27 Å while for the two-dimer cluster Si15H16 they obtained α = 15°, ΔE = 1.5 kcal/mol (0.07 eV) per dimer and d = 2.33 Å. The two research groups use different relaxation constraints and basis sets. This could explain the differences, given that a delicate balance of several effects is responsible for the ground state configuration of the Si9H12 cluster.

In the present study, the ground state of the clusters is determined in a two-step procedure. In the first step, the Si dimers are tilted as a whole, while keeping the other cluster atoms fixed and preserving the length of the dimer backbonds. We sample the total energy as a function of the dimer buckling angle α. The results for LDA and the PW91 functional are shown in Fig. 2. They are summarized in the ‘pre-relaxation’ column of Table 2 for all functionals used in the calculations.

The ΔE vs. α curves are mainly affected by the cluster size, rather than by the approximation used for ex-
The electronic structure of the cluster is influenced substantially by the dimer buckling. As a measure of the differences, we report the splitting between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the cluster, $E_g$, in the right column in Fig. 3. For Si$_{3}$H$_{12}$ $E_g$ is a monotonically increasing function of $\alpha$. It reaches its maximum for the largest used value of $\alpha = 20^\circ$, where the two dimer silicon and the two second layer neighbors of the buckled-down Si atom are almost coplanar. We attribute the opening of the HOMO-LUMO gap to changes in the symmetry character of the orbitals. While at $\alpha = 0$ the HOMO and LUMO orbital correspond to the $\pi$ and $\pi^*$ orbital of the Si dimer, they gradually develop into orbitals localized at one side of the Si dimer for increasing $\alpha$. The orbital at the lower Si atom acquires more $p$-character and is lifted in energy, while the orbital at the higher Si atom gets more $s$-character and is energetically lowered. With increasing cluster size $E_g$ is strongly reduced, while the dependence on $\alpha$ is almost unchanged. For the larger clusters we observe that the HOMO (LUMO) wave functions are no longer localized at a single Si atom, but are linear combinations of the dangling orbitals of all the buckled-up (buckled-down) Si atoms of the cluster. In the Si$_{21}$H$_{20}$ cluster, this leads to a splitting of the HOMO and LUMO levels into symmetric and antisymmetric states with respect to the mirror plane in the cluster. Thus this cluster reflects already to some extent the dispersion of surface bands observed in the slab. We expect that these changes in the electronic structure will also be reflected in the chemical reactivity, i.e., in the adsorption barrier $E_{ads}$ for H$_2$ molecules. It appears that a representation of the surface band structure on the cluster level is required for a correct description of the reaction energetics.

![FIG. 3. Top view of the Si$_{21}$H$_{20}$ cluster frontier orbitals. The contour plots are taken in the (001) plane 0.9 Å above the buckled-up Si atom of the middle dimer (dimers are denoted by shaded circles). The wave functions are real-valued. Full (dashed) contour lines indicate positive (negative) sign.

Relaxing the first and second silicon layers does not qualitatively change the results from the pre-relaxation study. However, the ground state energy and geometry differ substantially. The buckled dimer configurations of the Si$_{15}$H$_{16}$ and the Si$_{21}$H$_{20}$ clusters are now more stable by 1.5–3 kcal/mol (0.07–0.13 eV) and 3.5–4.5 kcal/mol (0.15–0.20 eV) per dimer, respectively. The HOMO-LUMO gap is found to decrease with increasing cluster size. The reduction can be partly attributed to a splitting of both the HOMO and LUMO state due to linear combinations of dangling bonds at neighboring Si dimers in the larger clusters (see Fig. 3). However, a

### TABLE I. Parameters of the clusters and the slab for different exchange-correlation functionals; the energy favor for buckling $\Delta E$ is given in kcal/mol per dimer and the gap $E_g$ between HOMO and LUMO in eV. $d$ refers to the Si-Si dimer bond length in Å and $\alpha$ to its buckling angle in degrees.

|        | Pre-relaxation | Two layers relaxed |        | Pre-relaxation | Two layers relaxed |        |
|--------|----------------|--------------------|--------|----------------|--------------------|--------|
|        | $\alpha$ | $\Delta E$ | $E_g$ | $\alpha$ | $\Delta E$ | $E_g$ | $d$ |
| LDA    |          |          |      |          |          |      |     |
| Si$_0$ | 4       | 0.1      | 1.00 | 6.9      | 0.1      | 1.18 | 2.21 |
| Si$_{15}$ | 8     | 0.8      | 0.59 | 15.7     | 2.7      | 0.86 | 2.28 |
| Si$_{21}$ | 10    | 2.0      | 0.40 | 18.6     | 4.0      | 0.70 | 2.35 |
| slab   | 12      | 1.9      |      | 18.9     | 4.5      |      | 2.35 |
| BP     |          |          |      |          |          |      |     |
| Si$_0$ | 0       | —        | 0.99 | 0        | 0.96     | 2.27 |     |
| Si$_{15}$ | 6     | 0.4      | 0.54 | 15.3     | 2.6      | 0.86 | 2.37 |
| Si$_{21}$ | 8     | 1.4      | 0.33 | 18.1     | 4.4      | 0.78 | 2.47 |
| slab   | 10      | 1.3      |      | 18.6     | 5.1      |      | 2.46 |
| PW91   |          |          |      |          |          |      |     |
| Si$_0$ | 2       | 0.0      | 0.96 | 4.9      | 0.1      | 1.10 | 2.24 |
| Si$_{15}$ | 6     | 0.5      | 0.43 | 15.7     | 3.1      | 0.88 | 2.32 |
| Si$_{21}$ | 8     | 1.7      | 0.33 | 18.0     | 4.6      | 0.74 | 2.40 |
| slab   | 10      | 1.5      |      | 18.3     | 5.1      |      | 2.40 |
| BLYP   |          |          |      |          |          |      |     |
| Si$_0$ | 0       | —        | 1.02 | 0        | 0.99     | 2.27 |     |
| Si$_{15}$ | 4     | 0.1      | 0.51 | 12.2     | 1.6      | 0.72 | 2.33 |
| Si$_{21}$ | 6     | 0.8      | 0.27 | 16.6     | 3.5      | 0.72 | 2.44 |
| slab   | 10      | 0.8      |      | 16.6     | 4.7      |      | 2.43 |

$^a$ $\alpha$ and $d$ for the Si$_{12}$H$_{20}$ cluster correspond respectively to the buckling angle and bond length of the middle dimer.
decrease is also observed, in particular at \( \alpha = 0 \), for a suitably averaged gap \( \langle E_g(\alpha) \rangle \), defined as

\[
\langle E_g(\alpha) \rangle = \frac{1}{N} \sum_{j=0}^{N-1} [E_{\text{LUMO}+j}(\alpha) - E_{\text{HOMO}+j}(\alpha)],
\]

where \( N \) is the number of dimers in the cluster. The reduction of the gap must be attributed to a weakening of the \( \pi \)-bonding with increasing cluster size. As could be anticipated, \( \text{Si}_{21} \text{H}_{20} \) gives closest agreement with the five-layer \( p(2 \times 2) \) slab. The \( \text{Si}_9 \text{H}_{12} \) cluster, on the contrary, is not large enough to model the properties of the clean Si(001)-(2 × 1) surface. Buckling in this case is strongly influenced by relaxation constraints and the approximation to exchange and correlation. While for the two larger clusters all functionals used here give similar results, their predictions for the \( \text{Si}_9 \text{H}_{12} \) ground state symmetry are qualitatively different. Though LDA and PW91 favor buckling with \( \alpha \approx 7^\circ \) and \( 5^\circ \), respectively, \(|\Delta E|\) is too small \( (\sim 0.1 \text{ kcal/mol}) \) to allow us to conclude unequivocally about the \( \text{Si}_{9} \text{H}_{12} \) cluster symmetry.

For the two-dimer \( \text{Si}_{15} \text{H}_{16} \) cluster using the BLYP functional we get \( d \) and \( \Delta E \) values identical to those of Konečný and Doren, but their predicted \( \text{Si}_9 \text{H}_{12} \) geometry is at variance with ours. Possibly the overestimation of the surface relaxation due to the absence of any geometric constraints in Ref. 39 is more crucial for the \( \text{Si}_{9} \text{H}_{12} \) cluster than for the larger ones.

At our imposed relaxation constraints the BP and BLYP functionals are found to give results for \( \text{Si}_{9} \text{H}_{12} \) in agreement with the CI methods. For the \( \text{Si}_{15} \text{H}_{16} \) cluster, however, buckling is always energetically favorable within DFT, whereas recent multi-reference CI calculations find the symmetric cluster to be lowest in energy. At present it is not clear if this is due to a lack of the CI calculations to recover the full correlation energy, or due to an inadequacy of the exchange-correlation functionals we are using. For the largest \( \text{Si}_{21} \text{H}_{20} \) cluster, we are not aware of CI calculations addressing the dimer buckling.

IV. REACTION ENERGETICS

The energetics of dissociative adsorption and associative desorption of \( \text{H}_2 \) is characterized by three points along the reaction pathway, the energies of the structures corresponding to the monohydride phase \( E_{11} \), the transition state energy \( E_{\text{TS}} \) and the sum of bare cluster energy \( E_{00} \) and that of the free \( \text{H}_2 \) molecule. Hence, the quantities of interest are defined by the differences

\[
\begin{align*}
E_{\text{ads}}^a &= E_{\text{TS}} - (E_{00} + E(\text{H}_2)), \\
E_{\text{des}}^a &= E_{\text{TS}} - E_{11}, \\
E_{\text{rxn}} &= E_{00} + E(\text{H}_2) - E_{11}.
\end{align*}
\]

The monohydride geometry of each cluster is obtained by saturating the dangling bonds of one Si dimer with H atoms. The equilibrium Si-H bond is 1.52 Å within LDA, PW91 and BLYP. When using the BP functional a bond length larger by 0.03 Å is obtained. The changes in \( d \) of the hydrogenated dimer are mainly governed by the approximation to the exchange and correlation, while the cluster size accounts only for differences of \( \sim 0.01 \text{ Å} \) for a given functional. We note that our TS and monohydride structures imply reaction of a single \( \text{H}_2 \) molecule with the Si(001) surface. For comparison to experimental data taken at finite hydrogen coverage, information about the coverage dependence of the energetics is also required. A single \( \text{H}_2 \) molecule per \( p(2 \times 2) \) unit cell in the extended slab case corresponds to a coverage of \( \Theta = 0.5 \) monolayers (ML). To assess the coverage dependence of the reaction energy \( E_{\text{rxn}} \), test calculations were carried out for a completely covered slab, \( \Theta = 1 \text{ ML} \). To obtain a better understanding of the role of buckling for the reaction energetics, we also performed test calculations for the symmetric \( p(2 \times 1) \) reconstructed Si(001) surface as possible reference of the clean surface. We note that the occupation of adjacent Si dimers by hydrogens could have a (probably small) influence on the transition state geometries and energies via interaction with the neighboring monohydride. This effect can be studied to some extent with the help of the two- and three-dimer clusters, which allow for adjacent doubly occupied Si dimers.
To get some insight into the influence of neighboring monohydrides on the asymmetric TS, we have performed calculations with Si$_{15}$H$_{16+x}$ and Si$_{21}$H$_{20+x}$ clusters with $x = 4$ and 6, respectively.

In this study, we concentrate on the pre-pairing scenario for the H$_2$ reaction with the Si(001) surface. Consequently, we locate the asymmetric TS of H$_2$ desorption from a single Si dimer for all clusters and functionals used in this study. In principle this can be achieved by mapping out the related potential-energy surface (PES), like e.g. in Ref. [15]. As an example, the potential energy as a function of the distance between the two H atoms and the H$_2$-cluster distance $Z$ is shown in Fig. 4. For each configuration of the two H atoms, the Si atoms in the two topmost layers have been relaxed. They follow ‘adiabatically’ the motion of the H atoms. Thus we make sure that the lowest possible TS in the multidimensional space of all mobile atomic coordinates is found. An alternative and generally faster approach uses a search algorithm, thus avoiding the need to map out all the points in the PES. All degrees of freedom of the H$_2$ molecule and the topmost two cluster/slab Si layers are included in the search. The ridge method implemented here starts from a pair of coordinates $x_0$ and $x_1$ in the multidimensional configuration space of the system, which denote the reactants (H$_2$ above the bare surface) and the products (the monohydride), respectively. An iterative search is then performed by halving the interval $[x_0, x_1]$ in each step. To reduce the number of required steps, we have shifted the input coordinates towards some initial guess $(x_0', x_1')$ closer to the TS. A projection of the search path onto a two-dimensional slice of the coordinate space is shown in Fig. 4 for the Si$_9$H$_{12+2}$ cluster within LDA. As seen, there is excellent agreement between the two schemes.

The geometries of the calculated TS are collected in Table II. As expected, the H-H bond is stretched in the asymmetric TS configuration of all Si$_x$H$_{y+2}$ clusters, with $R_{HIH}$ being largest for dissociation on the Si$_{21}$ cluster. As a consequence, the atom H2 at the transition state is by 0.2–0.3 Å closer to the buckled-up Si2 atom as compared with the Si9 cluster. The presence of two H atoms over the Si1 site partially blocks the mechanism that leads to anticorrelated dimer buckling and therefore $\alpha_{2s} < \alpha$. For the Si$_{21}$ cluster the unoccupied dimers are somewhat affected by the adsorption event, but their buckling angle $\alpha'$ is only a few degrees smaller than that of the clean surface. This small change is due to the dimer row termination by hydrogens in the clusters, and is absent in the slab geometries, where $\alpha' \approx \alpha$.

![FIG. 5. H$_2$/Si(001) reaction energetics as a function of the size of the system used to model the Si(001)-2×1 surface (see also Table III).](image-url)

Most noticeable in the results shown in Fig. 4 (numerical values are compiled in Table III) is a clear dependence of $E_{ads}$, $E_{des}$ and $E_{rxn}$ on cluster size. The...
common trend for all functionals is an effective flattening of PES along the reaction path with increasing cluster size. Both the reaction energy and the adsorption barrier are reduced. In general, for all clusters considered here, LDA gives a lower bound for the activation barriers and an upper one for $E_{\text{rxn}}$. For a given size of the cluster, we can compare the effect of the exchange-correlation functional employed in the calculation. As far as $E_{\text{rxn}}$ is concerned, all gradient-corrected functionals behave in a very similar way (see bottom panel of Fig. 5). This gives credibility to the statement that gradient-corrected DFT yields an accurate description of reaction energies. The quantities $E_{\text{ads}}$, $E_{\text{des}}$, involving transition state energies, show a stronger variation. The differences between BP and PW91 are only $\sim2$ kcal/mol, with the sign depending on the size of the system. The BLYP functional gives the highest value for $E_{\text{ads,des}}$ of all tested functionals. Since similar performance has been already established for small systems, our calculations confirm these results for extended clusters and slabs. The Si$_{12}$ cluster displays both the lowest adsorption and desorption barriers. Comparison between this cluster and the slab shows that their predictions agree to within $\sim3$ kcal/mol for all quantities. We conclude that the Si$_{12}$ cluster gives a fair description of the Si(001) surface, while the others are inadequate approximations for the surface. While the desorption barriers derived from the Si$_{12}$ cluster are in the range of 56 $\pm$ 3 kcal/mol for all functionals, $E_{\text{ads}}$ is more sensitive to the functional used, with values covering a range of 11 kcal/mol. The adsorption barriers derived from the gradient-corrected functionals using this cluster are 7–11 kcal/mol higher than the LDA barrier. This is in accord with the established picture that LDA tends to underestimate adsorption barriers at surfaces.

We note that the Si$_{13}$ cluster yields higher barriers for the PW91 functional than for BP, while the slab calculations give the opposite result.

It is instructive to analyze why the smaller Si$_9$ and Si$_{15}$ clusters give a poor description of the physics at the Si(001) surface, despite the fact that the Si–H bond is localized and should therefore be well represented already in the smallest cluster used. For $E_{\text{rxn}}$, the variation with cluster size is mainly due to differences in the bare quantities that accompany dimer buckling has also been emphasized in recent first principles studies of H$_2$O, C$_2$H$_2$, BH$_3$, and 1,3-cyclohexadiene reactions with the Si(001) surface. As our calculations show, the HOMO-LUMO gap $E_g$ is substantially reduced when going from the (mainly $\pi$-bonded) Si dimer in Si$_9$ to the surface band states in the slab. At the transition state for adsorption, the H$_2$ molecular orbitals, in particular the antibonding $^3\Sigma_u$ orbital, mix with both the HOMO and LUMO orbital, which is facilitated by a small $E_g$. At the TS of the Si$_9$ cluster, the H$_2$ mainly interacts with

| TABLE III. Activation and reaction energies in kcal/mol (eV) per molecule for H$_2$ adsorption/desorption on Si(001)-2×1 surface via pre-pairing mechanism (ZPE not included). |
|---|---|---|---|
|   | $E_{\text{ads}}$ | $E_{\text{des}}$ | $E_{\text{rxn}}$ |
| LDA |     |     |     |
| Si$_9$ | 10.2 (0.44) | 64.9 (2.81) | 54.7 (2.37) |
| Si$_{15}$ | 5.7 (0.25) | 58.4 (2.53) | 52.7 (2.29) |
| Si$_{12}$ | 3.5 (0.15) | 53.1 (2.30) | 49.6 (2.15) |
| slab | 0.9 (0.04) | 49.0 (2.12) | 48.1 (2.09) |
| BP |     |     |     |
| Si$_9$ | 18.1 (0.78) | 67.3 (2.92) | 49.3 (2.14) |
| Si$_{15}$ | 13.3 (0.56) | 61.4 (2.66) | 48.1 (2.09) |
| Si$_{12}$ | 10.2 (0.44) | 53.9 (2.34) | 43.8 (1.90) |
| slab | 11.6 (0.50) | 53.4 (2.32) | 41.8 (1.81) |
| PW91 |     |     |     |
| Si$_9$ | 15.9 (0.69) | 66.0 (2.86) | 50.1 (2.17) |
| Si$_{15}$ | 14.8 (0.64) | 63.0 (2.73) | 48.2 (2.09) |
| Si$_{12}$ | 12.0 (0.52) | 56.7 (2.46) | 44.7 (1.94) |
| slab | 9.6 (0.42) | 52.5 (2.28) | 42.9 (1.86) |
| BLYP |     |     |     |
| Si$_9$ | 20.2 (0.88) | 72.8 (3.16) | 49.7 (2.16) |
| Si$_{15}$ | 15.8 (0.69) | 64.6 (2.80) | 48.8 (2.12) |
| Si$_{12}$ | 14.5 (0.63) | 58.8 (2.55) | 44.3 (1.92) |
| slab | 15.5 (0.67) | 58.4 (2.53) | 42.9 (1.86) |

FIG. 6. Total valence electron density $n(r)$ (grey shading) and the density difference $\Delta n(r)$ (contour plot) in the plane containing H$_2$ molecule and the Si-Si surface dimer at the TS geometries of the Si$_9$H$_{2+2}$ (a) and the Si$_{13}$H$_{2+2}$ cluster (b) calculated with the PW91 functional. Density difference is defined by $\Delta n(r) = n(r) - n_{\text{clust}}(r) - n_{\text{H}_2}(r)$. The full contour lines correspond to $\Delta n > 0$ and dashed lines to $\Delta n < 0$. The plot levels are the same for both clusters.
TABLE IV. Coverage dependence of the reaction energy $E_{\text{rxn}}(\Theta)$ for the slab.

| $E_{\text{rxn}}(\Theta)$, kcal/mol (eV) per H$_2$ | 0.5 ML | 1 ML | 1 $\rightarrow$ 0.5 ML |
|-----------------------------------------------|--------|------|----------------------|
| LDA                                           | 48.1 (2.09) | 49.7 (2.16) | 51.3 (2.22) |
| BP                                            | 41.8 (1.81) | 43.8 (1.90) | 45.7 (1.98) |
| PW91                                          | 42.9 (1.86) | 44.7 (1.94) | 46.5 (2.02) |
| BLYP                                          | 42.9 (1.86) | 44.3 (1.92) | 45.7 (1.98) |

We have presented a systematic ab initio study of the H$_2$/Si(001) reaction energetics employing three clusters in plane-wave DFT calculations. A five-layer $p(2 \times 2)$ slab was used as a reference to analyze the convergence of the cluster predictions. All calculations were performed within LDA and with the non-local BP, PW91 and BLYP exchange-correlation functionals. As our results show, a conservative conclusion can be drawn that the most frequently used Si$_9$H$_{12}$ cluster is not large enough either to model the properties of the bare Si(001) surface or the molecular H$_2$ dissociation on it. The latter stems from the fact that this cluster is not capable of recovering the surface electronic structure. Though the H$_2$ reaction with the Si(001) surface is considered to be a highly localized event, non-local effects enter the reaction energetics via their influence on the surface bands. Hence, one could also expect different performance for the various functionals.

Our analysis shows that the quality of a given exchange-correlation functional should not be assessed without referring to the particular size of the cluster employed to study the H$_2$/Si(001) adsorption/desorption process. Indeed, it is evident, by inspecting the BLYP section of Table II for example, that one could infer for the Si$_9$ cluster an activation barrier to desorption much higher than the experimental values. Hence, as usually proceeded, the pre-pairing mechanism could be ruled out on energetic grounds. Such a conclusion, however, seems to be premature if one refers to the slab or, eventually, the Si$_{21}$ cluster prediction within the same functional.

In contrast to the one-dimer cluster approximation, the Si$_{12}$H$_{20}$ cluster was found to be close in its predictions to the slab calculations in all aspects of the reaction considered. With $E_{\text{ads}}^\text{des} = 56 \pm 3$ kcal/mol it is also well within the range of the experimentally determined desorption barriers. The relatively large spread in the calculated energies comes from the functionals used, with the BLYP functional giving the largest value for $E_{\text{ads}}^\text{des}$. ZPE corrections were not considered, but as they amount to a few kcal/mol at most and are essentially the same for different functionals, no qualitative change of our results is expected upon their inclusion. Concluding, our findings suggest that the effect of the cluster size in modeling the H$_2$ reaction with the Si(001) surface is significant and some of the previous works may well need a revision.

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1 For a nice review see D. J. Doren, Advances in Chemical Physics, edited by D. Prigogine and S. A. Rice (Wiley, New
