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Adsorption of hydrogen atoms on the silicon(111) (1×1) surface: first-principles calculations

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Abstract. With a first-principles method, the energy surface of hydrogen atoms diffusing on the silicon(111) (1×1) surface and the energy curves of H atoms approaching the Si(111) (1×1) surface from three high-symmetry sites were calculated. The three high-symmetry sites (denoted as the T1, T4 and H3 sites) correspond to positions on top of the first (T1), second (T4) and fourth (H3) layers of the Si atoms. It was found that two of the high-symmetry sites (T4 and H3) correspond to local maxima on the adsorption energy surface while the third one (T1) is the chemisorbed site, i.e. that with the lowest adsorption energy. The completely different characteristics for the three sites of the same symmetry are related to how much the charges transfer from the surface dangling bonds to the H atoms in the adatom structures. It was also found that no local minimum exists on the energy surface and that there is a saddle point. When the coverage varies from one monolayer to $\frac{1}{2}$ or $\frac{1}{4}$ monolayer, the changes in the adsorption energies for H atoms adsorbed at the three high-symmetry sites are, at most, around 0.2 eV/H. Finally, the energy curves for H atoms approaching the Si surface through the T1 and T4 sites exhibit the familiar strong repulsion near the surface. However the energy curve is soft through the H3 sites even when there is already one monolayer coverage of H atoms at the T1 sites of the surface. The energy barrier for H atoms to penetrate into the bulk through the H3 sites is not larger than 0.3 eV. The large negative formation energies for H atoms residing at several locations beneath the surface demonstrate that penetration of the H atoms into the bulk can easily occur.

1. Introduction

The interaction of hydrogen atoms with silicon surfaces has been studied over decades as H is not only a prototypical adsorbate but also a ubiquitous adsorbate on Si surfaces during various surface reactions. It is well known that H atoms can be easily adsorbed on Si surfaces up to a monolayer and passivate the surfaces by bonding to the dangling bonds of surface Si atoms (Schulze and Henzler 1983, Kobayashi *et al* 1983, Higashi *et al* 1990, Trucks *et al* 1990). Probably the most studied system is the Si(111) surface with chemisorbed H. During the adsorption of H atoms, the Si(111) (2×1) reconstruction of the freshly cleaved (111) surface is unreconstructed to form the (1×1) bulk-terminated surface (Becker *et al* 1990, Ancilotto and Selloni 1992). The critical H coverage to trigger the transition was found to be around 0.3–0.5 monolayers (Greenlief *et al* 1989, Ancilotto and Selloni 1992), which indicates that the Si surface bonds are strongly affected by the presence of the chemisorbed H. The adsorption process continues after the transition until one-monolayer coverage of H atoms is achieved. Despite the apparent simplicity of the H-chemisorbed Si(111) (1×1) surface, the system is regarded as one of the most basic and fundamental systems to be studied for chemisorption processes. Its detailed theoretical

investigations can lead to better understanding of other more complicated but structurally related systems.

The interaction energies between H and Si surfaces have always been regarded as an important source in understanding chemisorption processes. The interaction energies include the energy surface for the H diffusing on the Si surface and the energy curves for the H approaching the surface. With knowledge of the interaction energy, many properties of the chemical reaction in the dynamics of adsorption and desorption can be deduced from the appropriate Monte Carlo simulations (NoorBatcha *et al* 1985, Raff *et al* 1986 and Rice *et al* 1987, 1988). However there are not many reliable data available for the interaction energy. Usually a few data calculated with an *ab initio* method are used in the simulations together with guessed values. The results of the simulations therefore depend strongly on the guessed data, which are usually connected with assumptions on the characters of bonding between adatoms and the surfaces.

In this paper we present studies of the adsorption of H atoms on the Si(111) (1×1) surface using the *ab initio* density functional method (Hohenberg and Kohn 1964) with the local density approximation (Kohn and Sham 1965).

The Si(111) (1×1) surface contains three threefold-symmetry sites which correspond to positions directly above the first, the second and the fourth layer of Si atoms (figure 1). They are denoted as the T1, T4 and H3 sites respectively. The dangling bonds of the surface Si atoms make the T1 sites the perfect positions for bonding with H atoms. These are the chemisorbed positions for H atoms on the Si(111) (1×1) surface. Due to the high-symmetry characters, the T4 and H3 sites were assumed to be metastable positions for H atoms adsorbed on the Si(111) (1×1) surface, i.e. local minima on the adsorption energy surface in the Monte Carlo simulations of the chemisorption processes (Rice *et al* 1987, 1988, NoorBatcha *et al* 1985, Raff *et al* 1986). However, we shall show that instead of being local minima, the adsorption energies of hydrogen atoms at the T4 and H3 sites are actually local maxima on the interaction energy surface. The adsorption energy (E_{ad}) is defined as the energy difference between the adatom structure ($E_{ad,surf}$) and the sum of the energies of the ideal Si(111) (1×1) surface structure ($E_{ideal,surf}$) and the free H atoms (E_H):

$$E_{ad} = E_{ad,surf} - (E_{ideal,surf} + E_H). \quad (1)$$

To achieve high accuracy in the energy differences, all systems were taken with the same supercell and identical k point for the integration over the first Brillouin zone (for details, see section 2).

The energy surface of H atoms adsorbed on the Si(111) (1×1) surface was obtained by evaluating the adsorption energies on seventeen distinct positions of the irreducible zone of the surface (figure 1). It was found that no local minimum exists on the energy surface. The adsorption energies for H atoms adsorbed at the three high-symmetry sites at various coverages (one monolayer, $\frac{1}{2}$ monolayer and $\frac{1}{4}$ monolayer) were found to differ by less than 0.2 eV/H.

The interaction energy curves of H atoms approaching the Si(111) surface from directly above the T1, T4 and H3 sites were evaluated. That of the H3 site does not follow the conventional model, which proposes strong repulsion of the interaction energy curve near the surface. The adsorption path toward the H3 site is a possible channel for the penetration of H atoms into the Si bulk with an energy barrier of about 0.3 eV. This energy barrier does not increase even when one-monolayer coverage of H atoms at the T1 sites of the surface is present. The calculated formation energies of H atoms beneath the surface and the soft interaction energy curve of H atoms approaching the surface from directly above the H3

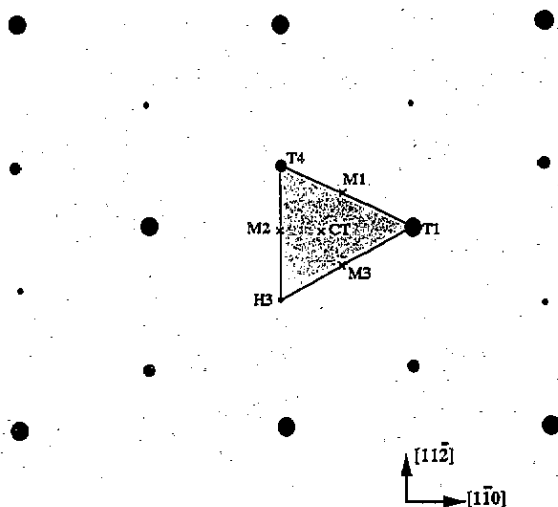


Figure 1. Top view of the Si(111) (1×1) surface. The large, medium and small dots correspond to the Si atoms of the first, second and fourth layers of the surface. Also indicated are seven of the seventeen selected sites whose H adsorption energies were calculated. The T1, T4 and H3 sites correspond to H atoms on top of the first-, second- and fourth-layer atoms of the surface. M1, M2 and M3 are the three positions in the middle of the lines connecting T1 and T4, T4 and H3 and H3 and T1 while the CT position is the centre of the irreducible zone (the shaded area) of the surface.

sites suggest that H atoms can easily penetrate into the Si bulk even when the surface is already covered with one monolayer of H atoms.

The calculational methods are described in the next section and the results and discussion are presented in the third section.

2. Calculational method

The calculations were based on the density functional theory (Hohenberg and Kohn 1964) with the local density approximation (Kohn and Sham 1965), and the Ceperley–Alder form (Ceperley and Alder 1980) was used to calculate the exchange–correlation energy. The norm-conserving pseudopotentials for the Si and H ions were taken from Bachelet *et al* (1982). Using the bare Coulomb potential for H ions gives only a small difference, i.e. 20 meV/H atom, in the adsorption energy. This was also confirmed in the paper of Chang and Chadi (1989).

All the structures in the calculations are periodic systems with slab configurations. The unit cells contain six double layers of Si along the $[111]$ direction with a period of nine double layers. The lattice constant used for Si is 5.40 Å, which is the theoretical lattice constant of Si at energy cut-offs (see below) of 10 Ryd. The adsorption energies calculated at $E_{\text{cut}} = 8$ Ryd (4 Ryd) using the theoretical lattice constants at 8 Ryd (4 Ryd) and 10 Ryd are different by less than 0.002 eV/H (0.03 eV/H). This value is smaller than the estimated maximum error bar (0.1 eV/H) from the convergence tests and can therefore be neglected. In calculating the energy of the free H atom, the corresponding unit cell, which consists of two evenly separated H atoms, is used. The shortest distance between these H atoms

is about 3.82 Å. The wavefunctions were expanded with plane waves and the calculations were performed in momentum space (Ihm *et al* 1979). For the Si(111) (1×1) surface structure, plane waves with kinetic energy up to 8 Ryd were included in the expansion and 25 k points in the first Brillouin zone, chosen with the scheme of Monkhorst and Pack (1976), were used. The convergence tests in the k -point sampling (using up to 64 points in the first Brillouin zone) and the energy cut-off (up to 10 Ryd) listed in table 1 show that the error bar of the adsorption energy is about 0.1 eV/H atom for the adatom structures with one monolayer coverage of H atoms on the Si(111) (1×1) surface. Similar tests were carried out in the calculations of structures with larger unit cells (for the $\frac{1}{2}$ and $\frac{1}{4}$ monolayer coverages of H adatoms) to achieve the same accuracy in the adsorption energy.

Table 1. Tests of energy convergence in the basis expansion and k -point sampling i.e. the integration over the first Brillouin zone. The energies (in units of eV/H atom) are the adsorption energies of H atoms on the T1, T4 and H3 sites with one-monolayer coverage. For the basis-expansion tests we considered calculations including plane waves with kinetic energies up to 4, 8 and 10 Ryd (energy cut-offs). For the k -point convergence, calculations with four k -point sets having 1, 9, 25 and 64 k points in the first Brillouin zone (according to the Monkhorst-Pack method) were performed.

$E_{\text{cut-off}}$ (Ryd)	Site	k point			
		1	9	25	64
4	T1	-2.696	-4.446	-4.508	-4.512
	T4	-2.042	-1.994	-1.981	—
	H3	-2.023	-2.221	-2.425	-2.425
8	T1	-3.213	-4.563	-4.602	—
	T4	-2.107	-2.021	-1.991	—
	H3	-2.049	-2.153	-2.368	-2.377
10	T1	-3.280	-4.510	-4.553	—
	H3	-2.085	-2.147	-2.349	—

3. Results and discussion

3.1. The energy surface for H atoms diffusing on the Si(111) (1×1) surface

For the Si(111) (1×1) surface structure, the irreducible zone is the equilateral triangle of the shaded area in figure 1. In order to obtain a thorough picture of the energy surface for H atoms moving on the surface, the adsorption energies of H atoms adsorbed at seventeen distinct sites in the irreducible zone of the surface were calculated. In addition to the three threefold-symmetry sites of T1, T4 and H3 mentioned in section 1, the M1, M2 and M3 sites, which are the middle points of the lines connecting every pair of the T1, T4 and H3 sites, and the CT site, which is at the centre of the equilateral triangle, were also selected. Six of the above seven sites, i.e. all except the CT site, are located on the same line along the $[1\bar{1}2]$ direction and their adsorption energies are plotted in figure 2. The adsorption energies along the direction $[1\bar{1}0]$ connecting T1 and M2 are shown in figure 3. As we shall show later that the M2 site is a saddle point on the energy surface, the adsorption energy of ten more distinct sites around it were also calculated.

Initially, the distance between the adatoms and the top surface layer was taken to be 1.48 Å, which is the bond length of SiH₄. The results are plotted with the solid line in

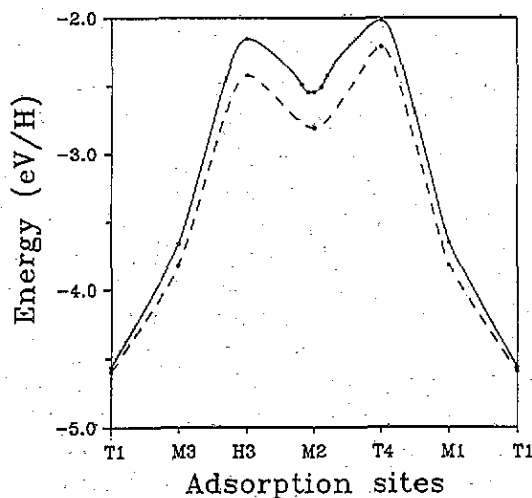


Figure 2. The calculated adsorption energies (in unit of eV/H atom) of H atoms adsorbed on the selected sites of the line along the $[11\bar{2}]$ direction (see figure 1). The asterisks on the solid and dashed lines correspond to the energies of the unrelaxed and relaxed adatom structures (see section 3.1 for details.)

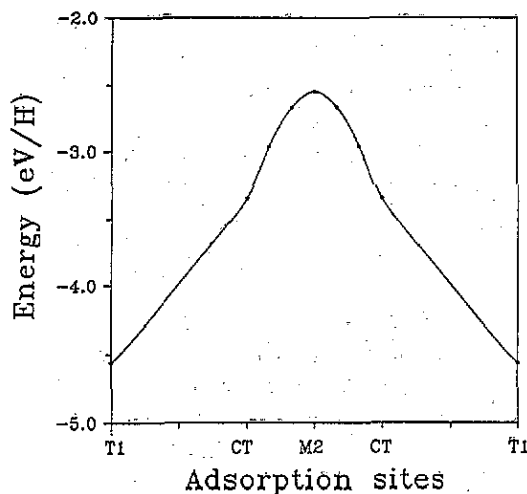


Figure 3. The calculated adsorption energies (in unit of eV/H atom) of H atoms on top of the Si(111) (1×1) surface along the T1 to M2 (i.e. $[1\bar{1}0]$) direction (see figure 1). All energies correspond to the unrelaxed structures.

figure 2. The adsorption energies of the relaxed structures were also calculated (the dashed line in figure 2). The adsorption energy curve did not change its main character when the structures were relaxed. In the calculations of the relaxed structures, the Si atoms of the top four Si layers and the adatoms were allowed to relax. These atoms were displaced until the forces on the atoms were less than 0.05 eV \AA . The adsorption energy for the T1 adatom structure changes little in the relaxation. The atomic forces were reduced quite significantly (from 0.8 eV \AA to 0.04 eV \AA) for the relaxed T1 adatom structure although

not much energy was gained. Our relaxed T1 adatom structure agrees with that calculated by Kaxiras and Joannopoulos (1988).

The T1 site, which is on the top of the surface Si atom with one dangling bond, was found to be the chemisorbed site, i.e. the site with the lowest adsorption energy, as expected. The calculated adsorption energy -4.5 eV/H is lower than that of the experimental result, which is -3.6 eV/H (Gupta *et al* 1988). This discrepancy could be due to the following contributions. Firstly, there is the zero-point motion of the H-Si bonds. For the stretching mode of the H-Si bond, the energy of the zero-point motion is about 0.1 eV (Jansson and Uram 1989). Secondly, if the very localized wavefunction of the free H atom were treated with the plane-wave expansion, it would considerably increase the magnitude of the adsorption energy. Thirdly, the local density approximation is well known to be unable to give the cohesive energies of solids with high accuracy as it is for other physical properties such as lattice constant, phonon frequency etc (see, for example, the paper by Li *et al* 1991). Although we cannot estimate the magnitude of the errors due to the second and the third effects, this is expected to occur more or less consistently on the adsorption energies and therefore will not bias our understanding and discussion of the calculated results.

One of the interesting results emerging from the calculations is that the adsorption energies of H atoms on the H3 and T4 sites are local maxima of the energy surface (figure 4). These two sites, like the T1 site, also exhibit threefold symmetry. From the conventional guess, the high-symmetry H3 or T4 site might also be bonding sites with smaller values of bonding energies than that of the T1 sites, i.e. corresponding to local minima of the adsorption energy surface. The conventional guess originates from the idea that the H atom adsorbed on the T4 or H3 site obtains a total of one electron dangling bond for bonding to the surface from the dangling bonds of the three nearest and equally oriented surface Si atoms. The threefold symmetry of the T4 and H3 adatom structures guarantees zero lateral force for the adsorbed H atoms and therefore might correspond to a local minimum of the energy surface. These assumptions have been used in the Monte Carlo simulation of H atoms diffusing on the Si(111) (1×1) surface (Rice *et al* 1988). However, our calculations show that the adsorption on the T4 and H3 sites actually corresponds to local maxima on the adsorption energy surface.

In order to investigate how the bondings are formed at different adsorption positions and their relations to the adsorption energy, the average charge density transfers of the adsorption were evaluated (figure 5). The average charge density of a point is referred to the average charge density of the area of a circle of radius 1.1 Å around the point and the circle is on the plane parallel to the Si(111) surface. The radius was chosen to be half of the distance between the nearest-neighbour atoms of the (111) atomic planes. Beyond this region the charge distribution difference is too small to affect the result. Averaging over a circular area with a radius of 0.6 Å gives similar qualitative results. In figure 5, the charge density transfers were obtained by subtracting the average charge densities of the Si(111) (1×1) surface structure and the free H atoms at the adatom sites from the average charge densities of the adatom surface structures. The points are located along the lines perpendicular to the surface and passing through the corresponding adatoms, i.e. T1, T4 and H3 sites. This clearly shows that the bonding between the H atoms and the surface Si atoms on the T1 sites is very ionic. The large transfer of charge from the Si dangling bonds to the H atoms leads to the much larger bonding energy for adsorption on the T1 site than for the T4 and H3 sites.

The calculations also show that there is no local minimum that can trap the H atoms on the energy surface. The energy surface has a global minimum at the T1 site and two local

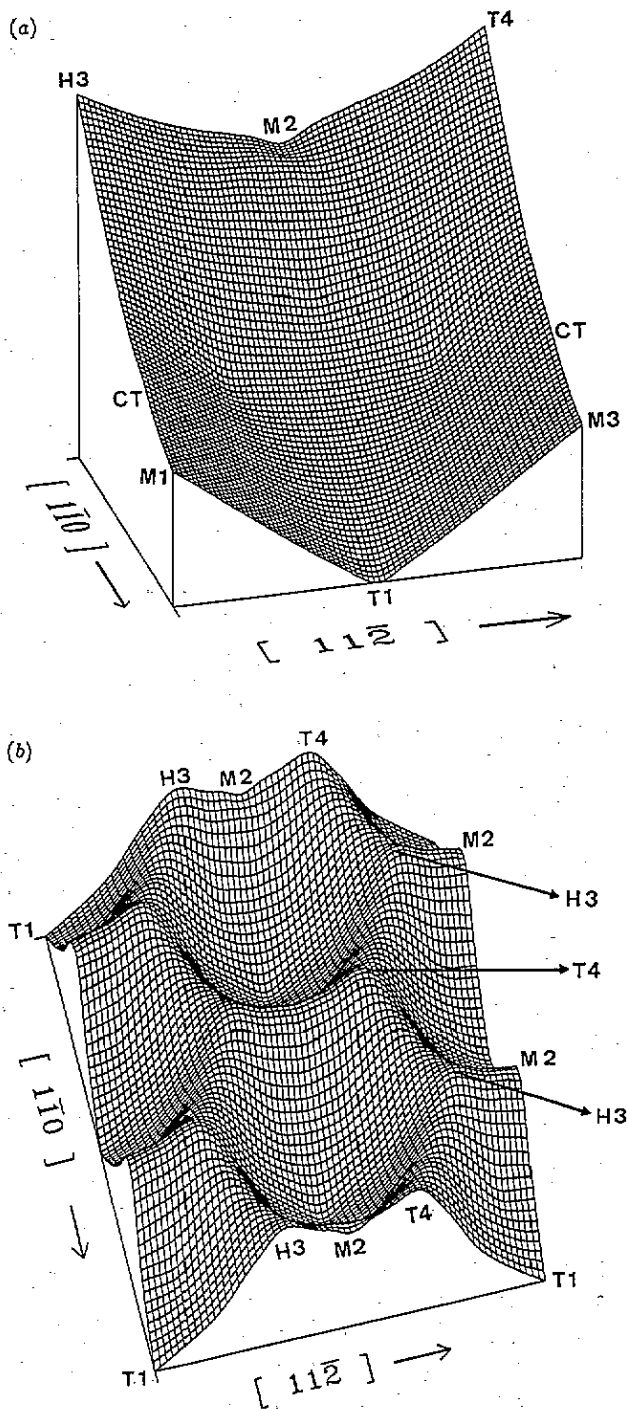


Figure 4. The energy surface for H atoms diffusing on the Si(111)-(1 × 1) surface. In (a) the energy surface for an area of twice the irreducible zone is plotted. One can see clearly the saddle point M2 of the energy surface. In (b) the energy surface for a large rectangular area of the surface (such as that of figure 1) is shown. The positions of different adsorption sites can be found in figure 1.

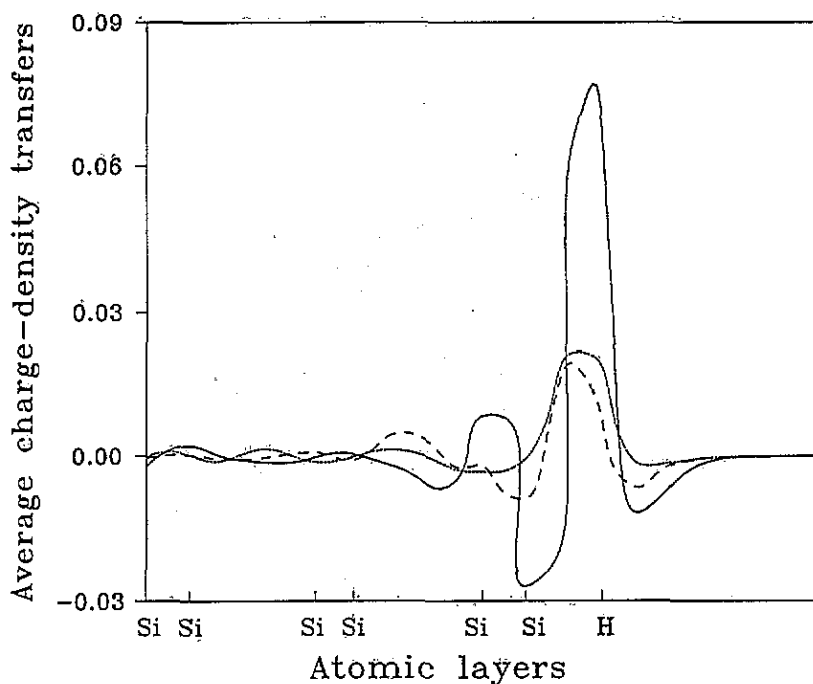


Figure 5. The average charge density transfers for the T1, T4 and H3 adatom structures. The charge density transfers were obtained by subtracting the charge densities of the Si(111) (1×1) surface structure and those of the free H atoms on the adatom positions from those of the adatom structures. The average charge density (defined in section 3.1) was then evaluated along the lines perpendicular to the surface and passing through the corresponding adatoms. The solid, dashed and dotted curves correspond to the average charge density transfers of the T1, T4 and H3 adatom structures, respectively. The charge density is in units of electronic charge \AA^{-3} and the positions of the atomic layers are indicated on the horizontal axis.

maxima at the T4 and H3 sites. In the centre of these minima and maxima is the saddle point M2 of the energy surface (figures 1-4).

3.2. The adsorption energies of T1, T4 and H3 structures at different H coverages

As the results of the previous section were all obtained with periodic systems containing one monolayer of H atoms, one would be sceptical of the validity of their application to the realistic adsorption process, i.e. the process that corresponds to the individual H atom being adsorbed onto the surface. To check this, we studied the adsorption of H atoms on the three high-symmetry sites, i.e. T1, T4 and H3, at $\frac{1}{4}$ -, $\frac{1}{2}$ - and one-monolayer coverages. The results are listed in table 2. Although the systems with $\frac{1}{4}$ -monolayer coverage were only calculated at the energy cut-off of 4 Ryd, it can be concluded by inspecting the calculated values that the energy difference between different coverages is, at most, around 0.2 eV/H atom. As mentioned in the introductory section, the cleaved (2×1) surface would transform to the (1×1) structure when the H coverage is more than 0.3 or 0.5 monolayers coverage. Our calculations show that once the transformation is completed, the energy surface for the H atoms diffusing on the Si surface follows closely the results we presented in the previous section.

Table 2. Adsorption energies of H atoms on the Si(111) (1 × 1) surface with 1, $\frac{1}{2}$ and $\frac{1}{4}$ monolayer coverage (θ) of H atoms at the T1, T4 and H3 sites. The 4 and 8 Ryd values correspond to the tests in the convergence of the basis set expansion.

$E_{\text{cut-off}}$ (Ryd)	Site	Coverage θ		
		1	$\frac{1}{2}$	$\frac{1}{4}$
4	T1	-4.508	-4.427	-4.603
	T4	-1.981	-2.101	—
	H3	-2.425	-2.449	-2.579
8	T1	-4.602	-4.540	—
	T4	-1.991	-2.120	—
	H3	-2.386	-2.511	—

3.3. H atoms approaching the Si(111) (1 × 1) surface

The energy curves of H atoms approaching the Si(111) (1 × 1) surface from directly above the surface sites of T1, T4 and H3 were evaluated (figure 6). The energies were calculated with one monolayer of H atoms in the system and without structural relaxations (the three curves with solid circle data). As the mass of the H atoms is considerably smaller than that of the Si atoms, the interaction energies of the unrelaxed structure are expected to be a good approximation for the approaching process.

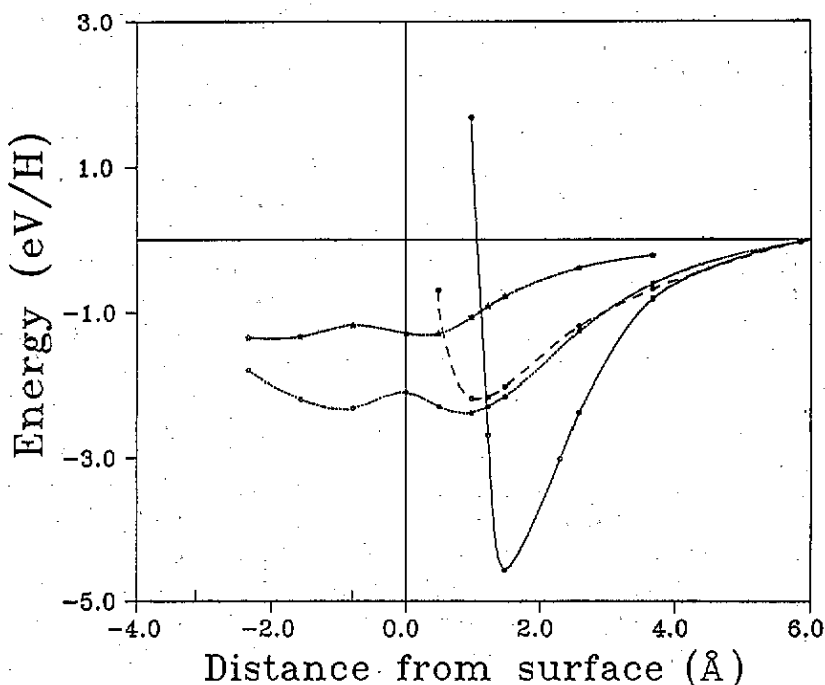


Figure 6. The interaction energies (solid circles) of H atoms approaching the Si(111) (1 × 1) surface from directly above the T1 (solid curve), T4 (dashed curve) and H3 (dotted curve) sites. The energy is in units of eV/H atom. The $x = 0$ line corresponds to the surface atomic layer. The positions of the second and third Si layers are indicated by ticks on the inside of the horizontal axis. The distances from the surface are in units of Å. Also presented in this figure (the dotted curve with asterisks) is the energy curve for H atoms approaching the surface from directly above the H3 positions while there is already one-monolayer coverage of H atoms on the T1 sites.

The energy curves of H atoms approaching the T1 and T4 sites are like the usual adatom-surface interaction energy curves, which show strong repulsion as the adatoms approach the surface after passing the energy minima. However, the interaction energy curve at the H3 site demonstrates that it is a possible path for H atoms penetrating into the bulk. The energy barrier for H atoms to penetrate into the bulk through the H3 path is about 0.3 eV. This soft potential energy is due to the empty space between the surface and the fourth atomic layer along the H3 path. If the H atoms enter the bulk through the H3 site and keep moving along the H3 path, they will finally encounter the same strong repulsion as on the T1 and T4 paths when they approach the Si atoms of the fourth atomic layer. However, if they do not follow the H3 path, there are other possible sites beneath the surface for the H atoms to remain. We shall show our calculated results later. Before we discuss our investigation of the formation energies for H atoms beneath the surface, the influence of the adsorbed H atoms on the possible penetrating energy curve is presented.

The dotted curve with asterisks in figure 6 is the interaction energy curve of H atoms approaching the H3 sites when the surface is already covered with one monolayer of H atoms at the T1 sites. The minimum of the energy curve is higher than that without one-monolayer coverage of H atoms, as expected. However, the energy curve is still soft and the energy barrier is small (about 0.1 eV). One might suspect that these results are due to the (1×1) cell used in the calculations, i.e. due to the strong interactions between H atoms. However, we have already shown in the last section that the interactions between H atoms are small at the three high-symmetry sites. For the positions beneath the surface along the H3 path, the calculations with the $2(1 \times 1)$ cell (i.e. $\frac{1}{2}$ -monolayer of H atoms beneath the surface) were also performed while the adsorption on the surface was still one monolayer. The values of the energies change by less than 0.2 eV/H from those calculated with the (1×1) cell. The adsorption of one monolayer of H atoms on the surface therefore does not prohibit the H atoms from penetrating into the bulk.

Now we shall show that there are locations beneath the surface in which H atoms can reside. The formation energies of several positions on the $[1\bar{1}0]$ plane and beneath the surface were evaluated and are shown in figure 7. The calculations were performed with one monolayer of H atoms in the system (the data *not* in parentheses in figure 7), while no structural relaxation was considered. The position beneath the surface that mirrors the T1 site above the surface has a formation energy of -3.3 eV for one H atom. This is lower than the adsorption energies of the H atoms on the T4 and H3 sites. The large value of the formation energy is due to the presence of the dangling bonds of the surface Si atoms. In addition to the site just below the surface T1 site, there are other sites whose binding energies for H atoms are of considerable magnitude. Apparently the interstitial area beneath the surface is full of attractive potentials for H atoms. For a site below the fourth atomic layer of the surface, the binding energy is -2.2 eV/H (see figure 7).

The formation energies of H atoms beneath the surface when the surface is already covered with one monolayer of H atoms at the T1 sites were also calculated and are presented in figure 7 (the data in parentheses). Although these formation energies are considerably smaller than those when the surface is not covered with H atoms, their magnitudes are not tiny. There have been many studies of systems with H atoms in the Si bulk (Nichols *et al* 1989, Chang and Chadi 1989, Bonapasta 1991). As we are mostly interested in the interactions of H atoms with the Si(111) (1×1) surface, we will not proceed any further in discussions on the studies of H atoms beneath the surface in the present paper. However, we have shown that the adsorption of H atoms on the Si(111) (1×1) surface will not stop after one-monolayer of H atoms, as H atoms can still easily penetrate into the bulk and remain there.

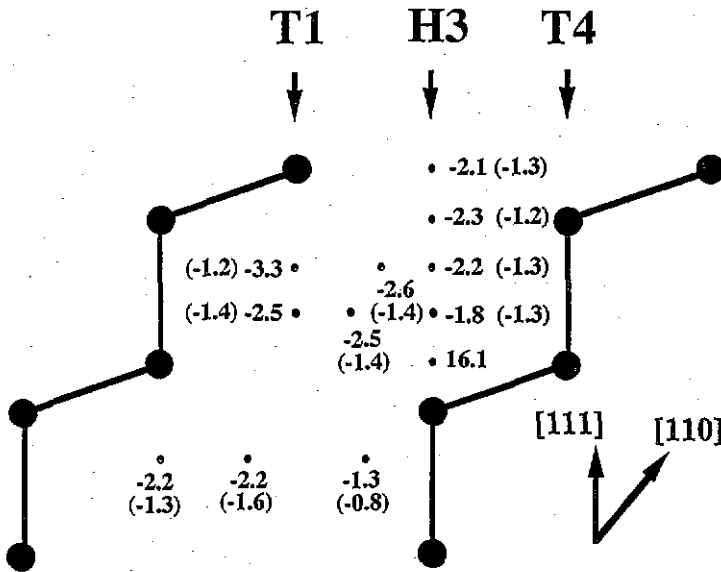


Figure 7. The formation energies for H atoms beneath the Si(111) (1×1) surface. The values with and without parentheses correspond to systems with and without one-monolayer coverage of H atoms at the T1 sites of the surface. The energies are in units of eV/H atom. The atomic plane is the $[1\bar{1}0]$ plane and the solid circles are the Si atoms. The T1, H3 and T4 sites are indicated.

4. Conclusions

We have carried our *ab initio* quantum mechanical calculations to study the adsorption of H atoms on the Si(111) (1×1) surface. The three high-symmetry sites, i.e. T4, H3 and T1, of the surface correspond to two local maxima and one global minimum on the energy surface. The completely different characters of the energy surface for the three high-symmetry sites are mainly due to the degree of charge transfer of the surface dangling bonds to the adsorbed H atoms. The energy surface was found to have no local minimum and have a saddle point. The energy surface is expected to change little as the coverage varies from $\frac{1}{4}$ to one monolayer. The path of H atoms approaching the surface through the H3 sites was found to be a possible channel for them to penetrate into the bulk with an energy barrier of 0.3 eV. This energy barrier does not increase after the surface is covered with one monolayer of H atoms at the T1 site. The H atoms can remain beneath the Si surface with formation energy as low as -3.3 eV/H or -1.6 eV/H. The two values correspond to systems without (-3.3 eV/H) and with (-1.6 eV/H) one monolayer coverage of hydrogen atoms at the T1 sites of the surface, while no relaxation energy was included.

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