

## Theoretical calculations of H interacting with Si(100) $1 \times 1$

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We have performed fully self-consistent calculations of the electronic properties of a monolayer of H interacting with a Si(100)  $1 \times 1$  surface in order to understand the chemisorptive properties of highly unsaturated Si surface atoms [Si (100)  $1 \times 1$  has two broken bonds per surface atom]. A total of eight separate geometries were studied, corresponding to Si-H separations ranging from 2.8 to 4.4 a.u. It was found that the Si monolayer had an equilibrium separation of 2.86 a.u. and an equilibrium force constant of  $k = 0.156$  a.u. The interaction potential between the H monolayer and the Si substrate was well fit by empirical interaction potentials of the Morse and Rydberg form, which implied a dissociation energy for the Si-H bond of 3.4 eV. The surface spectrum was also studied, the most interesting features of which were a Si-H bonding surface-state band similar in position to that found on Si(111), and a lone-orbital surface-state band, half occupied and essentially identical to the bridge bond state on clean Si(100).

### I. INTRODUCTION

We have carried out fully self-consistent calculations of the electronic properties of a hydrogen-covered Si(100)  $1 \times 1$  substrate.<sup>1</sup> The hydrogen atoms were assumed to be positioned directly over the Si surface atoms, at separations which ranged from 2.7 to 4.4 a.u. For all separations, of which there were a total of eight, the Si atoms were frozen at their ideal positions. The geometry specified here is not likely to correspond directly to an experimentally produced hydrogenated Si(100) surface.<sup>2</sup> We have chosen it rather for the following reasons. It allows us to understand the interaction of H with a realistically modeled Si substrate where the Si surface atoms have multiple broken bonds. These highly unsaturated Si atoms, while not present on the physical Si(100) surface, are associated with actual surface defect structures, such as steps,<sup>3</sup> on other Si faces. The chemisorption properties of these structures are of considerable importance.<sup>4</sup>

The large number of geometries studied allowed us for the first time to construct a potential-energy curve for a foreign atom interacting chemisorptively with a realistically modeled solid. An analysis of this potential and its interpretation in terms of model pairwise potentials commonly employed for diatomic molecules will be one of the primary results of this study.

The self-consistent calculations yield detailed spectral information for the chemisorbed system, which will be compared and contrasted with the previous results for H chemisorbed on Si(111).<sup>5</sup> That surface, in contrast to Si(100)  $1 \times 1$ , is completely saturated by the chemisorption of a monolayer of H, so one must expect that their spectra will be qualitatively different.

Another topic we shall touch upon is the effec-

tive charge transfer between the Si and H, its dependence on the distance between Si and H, and the effect of induced charge rearrangement *within* the substrate, which causes a significant change in substrate work function, independent of charge transfer between the chemisorbed species and the substrate.

### II. GENERAL METHODOLOGY

We have carried out self-consistent model potential calculations of the electronic structure of H covered Si(100) surfaces using our methods.<sup>6</sup> These calculations closely parallel those of Appelbaum, Baraff, and Hamann for the clean Si(100) surface,<sup>7</sup> and the reader is referred to these for a detailed discussion of the methods used in the present calculations.

The geometry of the surface is shown in Fig. 1. The open circles represent Si atoms in their ideal

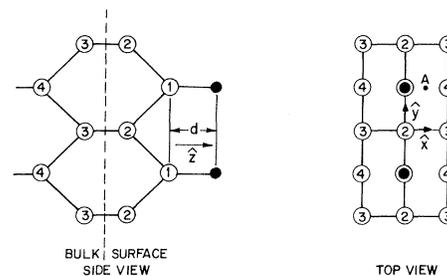


FIG. 1. Geometric structure of the H-covered Si(100)  $1 \times 1$  surface being studied in this paper. Open circles represent Si atoms; closed circles H atoms. The numbers within the open circles indicate the atomic planes to which the Si atoms belong, with the plane nearest vacuum labeled 1, next nearest 2, and so forth. The point denoted by A in the top view labels the position of a ray along which surface-state densities are plotted in Fig. 8(a).

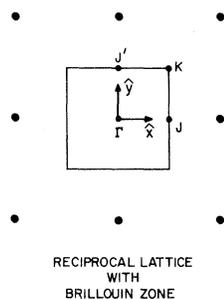


FIG. 2. Reciprocal lattice and surface Brillouin zone of the Si(100) surface is shown and the symmetry points of the latter are labeled.

undistorted geometry and the smaller filled circles represent the H atoms. These are constrained to lie right above the atoms of the last Si plane, with their distance  $d$  from these atoms allowed to vary between 2.7 and 4.4 a.u. The presence of the H monolayer leaves this surface with the same point group and translational symmetry as that of the clean ideal Si(100) surface. The surface Brillouin zone is shown in Fig. 2 with the symmetry point labeling previously adopted. For constructing a surface charge density the  $\Gamma$  and  $K$  point were used, in a fashion exactly analogous to the clean Si(100) surface calculations, for the filled bands. In contrast with the clean Si(100) surface, the gap surface-state band structure for the hydrogenated surface has a very simple form, with only one half-filled gap surface state band present for all H-Si separations. This made it unnecessary to use additional  $\bar{k}_{\parallel}$  points in treating this band and resulted in charge conservation comparable to that achieved for the clean surface.

Self-consistency in the potential achieved to better than 0.1 eV rms throughout the surface region, typically required three iterations per geometry. This efficiency was achieved with the use of linear response theory, which enabled us, in a manner similar to that described for clean Si(100),<sup>8</sup> to modify an already obtained self-consistent potential for a neighboring geometry, so it could be used as a highly accurate starting potential for the new geometry.

### III. INTERACTION POTENTIAL

The interaction between the H overlayer and the Si(100) substrate can be calculated from the self-consistent surface charge density most easily by using the Hellmann-Feynman theorem. The theorem states, in the context in which we apply it here, that the force on an atom is equal to the gradient, with respect to nuclear coordinate of the electrostatic and core pseudopotential energy,

TABLE I. The force  $F$ , on the H atoms in a.u. is tabulated vs Si-H distance  $d$  (in a.u.). A positive force corresponds to an attractive Si-H interaction.

$d$	Si-H force	$10^2 F$
2.68		-3.6
2.78		-1.5
2.88		0.3
3.20		3.6
3.80		5.8
3.90		5.5
4.10		5.3
4.40		4.8

holding the valence charge density fixed. The results of such calculations, for eight separate Si-H separations, are tabulated in Table I, while four of the eight surface charge densities used in these calculations are shown in Fig. 3. An examination of Table I indicates an equilibrium separation between the Si and H layers to be between 2.78 and 2.88 a.u. Quadratic interpolation of the forces at these points and 2.68 a.u. yielded for the equilibrium separation  $d$ , 2.86 a.u., and for  $k$ , the equilibrium force constant, 0.156 a.u. The calculated Si-H bond length and force constant are similar to those found for<sup>5</sup> H on Si(111) and fall within the range measured for Si-H bonds in a variety of molecules. It is further apparent from Table I that the restoring force on the H quickly becomes asymmetrical for displacements  $>0.2$  a.u. and this asymmetry clearly indicates the beginning of a hard core repulsion between the H and the Si substrate. For large positive displacements of the H away from the Si surface, restoring forces saturate, and in fact begin decreasing by 3.8 a.u. The behavior exhibited in Table I is typical of diatomic force laws. To examine this correspondence quantitatively we have fit the calculated forces to two well-known interaction potentials, due, respectively, to Morse and Rydberg<sup>9</sup>

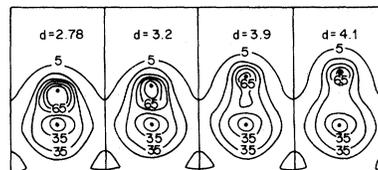


FIG. 3. Contours of constant-surface charge density are plotted on planes normal to the Si(100) surface, passing through the Si-H bond, and at right angles to the Si-Si bonds between the first- and second-layer Si atoms. Units are atomic, the density has been scaled by  $10^3$ .

$$V_M(z) = D_e(e^{-\beta(z-R_e)} - 2)e^{-\beta(z-R_e)} \quad (3.1)$$

and

$$V_R(z) = -D_e[1 + b(z - R_e)]e^{-b(z-R_e)}, \quad (3.2)$$

where  $R_e$  is the equilibrium bond length of the diatomic in question,  $D_e$  its dissociation energy, and  $\beta$  and  $b$  are stiffness parameters related to the harmonic spring constant  $k$  of the molecule by (Morse)

$$k = 2\beta^2 D_e \quad (3.3)$$

and (Rydberg)

$$k = b^2 D_e. \quad (3.4)$$

While the Morse form is perhaps the most well-known pairwise interaction potential, it is believed<sup>10</sup> that the Rydberg form offers an overall better fit to the interaction potential of a diatomic. Having chosen the form of the interaction potential, it is still necessary to specify which Si atoms the H atom interacts with. One assumption is that each H atom interacts at all separations with the single Si atom to which it is nominally bonded at equilibrium separations. The consequences of this assumption are exhibited in Figs. 4 and 5, in which, respectively, the Morse and Rydberg forms were used. It is seen that either provides an adequate fit to the calculated points, shown as heavy circles in the figure.

The global fit provided by either (3.1) or (3.2) indicates a somewhat stiffer force constant and essentially the same equilibrium separation as found by local interpolation of Table I. In addition, it provides a bonus in the form of the effective dissociation energy of the Si-H bond. This was determined to be either 3.9 or 4.0 eV, depending on whether the Rydberg or Morse form was used, and is comparatively close to, although somewhat higher than, the typical Si-H bond 3.2

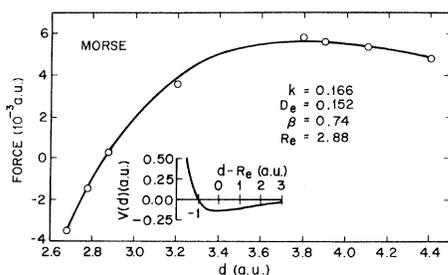


FIG. 4. Calculated force, open circles (a positive force is toward the surface) on the H surface are fit by a Morse form. The parameters of the fit are shown within the figure along with a plot of the Morse potential vs distance implied by that fit. All units are atomic.

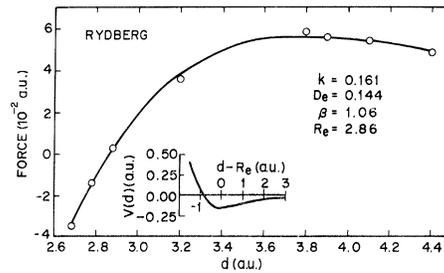


FIG. 5. Calculated force, open circles (a positive force is toward the surface) on the H surface are fit by a Rydberg form. The parameters of the fit are shown within the figure along with a plot of the Rydberg potential vs distance implied by that fit. All units are atomic.

eV. A direct check on the dissociation energy would be highly desirable, but the uncertainties of the surface energy associated with the clean Si(100), a consequence of its relatively complex surface band structure, and the general problem of small differences in large numbers, makes this comparison impossible at present. The assumption that a H atom interacts with only a single Si atom may be adequate when the H-Si separations are near equilibrium but it clearly is no longer true as the Si-H separations become large. Then each H is interacting with many Si atoms, not just the single Si to which it is normally bound. To explore this further we have assumed each that H interacts via (3.1) or (3.2) with all surface Si atoms. The quality of the fit we achieve with this assumption, shown in Fig. 6 and 7, is quite similar to that achieved by restricting the interaction to a single Si-H pair.

For the Rydberg fit, the stiffness and equilibrium separation parameters are essentially unchanged, while the effective dissociation parameter  $D_e$ , is reduced to 3.4 eV. Similar behavior was found for

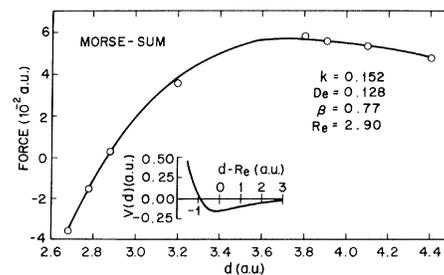


FIG. 6. Calculated force, open circles (a positive force is toward the surface) on the H surface, are fit by a sum of Morse potentials. The parameters of the fit are shown within the figure along with a plot of the sum of Morse potentials versus distance implied by that fit. All units are atomic.

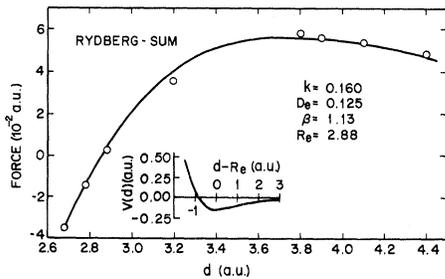


FIG. 7. Calculated force, open circles (a positive force is toward the surface) on the H surface, are fit by a sum of Rydberg potentials. The parameters of the fit are shown within the figure along with a plot of the sum of Rydberg potentials vs distance implied by that fit. All units are atomic.

the Morse fit.

It must be emphasized that the total dissociation energy for the H monolayer is essentially the same whether we assume only a single Si-H interaction or many pairwise attractions; only the inferred single Si-H bond strength is different. The 0.4-eV difference between a single Si-H bond and the average bond of an H monolayer bonded to a Si substrate appears to us to be reasonable.

#### IV. SURFACE SPECTRAL PROPERTIES

We begin our discussion of the H covered Si(100) surfaces studied here with a brief review of the spectral properties of the clean surface.<sup>7, 8, 11</sup> The two broken bonds present per surface atom on Si(100) result in two bands of surface states which lie within the band gap of bulk Si. One is dangling-bond-like, relatively narrow in energy, and almost completely filled. The other is almost empty, with a spatial distribution centered on the intersection of the last Si atomic plane and the plane containing the bonds broken in forming the surface. We refer to this as the bridge bond because of its role in surface reconstruction. It is essentially nonbonding in the ideal geometry studied here.

The presence of the H above the last Si plane strongly perturbs the dangling bond band. In its place one finds two bands of states that are derived from the 1s orbital of H (with  $p$  admixture) and the dangling orbital of Si. The spatial nature and energy of these orbitals depends sensitively on the Si-H separation. This is seen in Fig. 8 where the charge density of the Si-H bonding surface state at  $\vec{k}_{\parallel} = K$  is plotted along a line perpendicular to the surface and passing through a Si-H bond for two limiting Si-H separations studied. The antibonding counterpart of this surface state is seen in Fig. 9, for the larger of the two separations shown

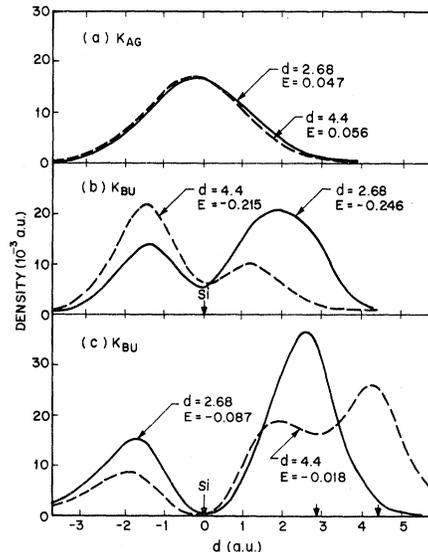


FIG. 8. Charge density for various surface state bands at  $\vec{k} = K_{AG, BU}$  (see Fig. 2) are plotted versus distance along rays normal to the surface. Note that the subscripts  $AG$  and  $BU$  refer to the point-group symmetry of the states, with  $AG$  states even under both mirror reflections, and  $BU$  states odd on reflection about the plane normal to the broken bonds. The various types of bands are shown for two Si-H separations,  $d = 2.68$  and  $4.4$  a.u., and their energies  $E$  are indicated in the figure. (All energies are in atomic units.) (a) The lone orbital surface band is shown along the ray passing through the point labeled A in Fig. 1. (b) A deep-lying surface band is shown along a ray through the Si-H bond. (c) The Si-H bonding surface state band is plotted along the Si-H bond. Arrows on the horizontal axis locate the H positions for the two geometries.

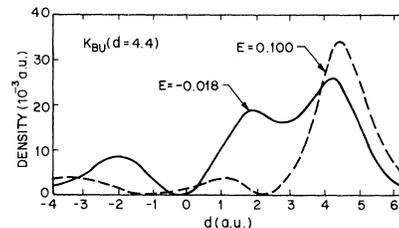


FIG. 9. Charge density of the antibonding Si-H surface state at  $\vec{k} = K_{BU}$  (dashed curve) is compared with that of its bonding counterpart for a Si-H separation of  $4.4$  a.u. The  $BU$  subscript indicates the state is odd on reflection in the plane normal to the broken bond direction and lying midway between surface atoms. The ray along which the charge density is plotted is normal to the surface and through the H. The energies of the states  $E$  are indicated in the figure (in a.u.).

in Fig. 8. This state, which is not occupied, was not monitored for smaller Si-H separation. With its energy for  $d=4.4$  already near the bottom of the conduction band, it is clear that the anti-bonding surface state is well within the conduction band for Si-H separations nearer equilibrium.

The behavior illustrated in Fig. 8(c) is a classic picture of covalent bond formation. The dangling-bond band, however, is completely filled on clean Si(100). To make room for the H donated electron the dangling-bond orbital must promote an electron into the bridge bond orbital. This orbital, empty for the clean surface, lies just above the dangling-bond orbital and accommodates quite naturally the promoted electron. Because the bridge bond orbital has, by symmetry, a nodal plane through the Si-H bond, its spatial character and energy are very insensitive to the H bonding. This is illustrated in Fig. 8(a), where the charge density for this state at  $\vec{k}_{\parallel}=K$  is plotted along a line normal to the surface and displaced from the surface atom along the broken bond direction by  $\frac{1}{4}$  of the distance between adjacent surface atoms. The location of this point is indicated in Fig. 1 by the label A. It was chosen so one could monitor the region of maximum charge density for this state. Notice that the state shifts little with Si-H separation, and its energy, referenced to the Si band structure, is close to that found for the clean surface. The bridge bond surface band acts then as a lone orbital, neither bonding nor antibonding in character, containing one electron. For simplicity we have used the  $\vec{k}_{\parallel}=K$  state to represent the charge in that band. Because the band is half filled it is clear that the  $1 \times 1$  surface with a monolayer of H is not stable to a surface metal-insulator phase change. If permitted, the H-covered surface would dimerize, as does the clean surface.

It is interesting to examine what we expect to happen for very large Si-H separations. At some point charge must begin to flow out of the bridge bond. This charge will flow into the antibonding Si-H state, which is dropping in energy and which ultimately goes over to the hydrogen  $1s$  state. The bonding state in turn, changes into the clean-surface dangling-bond band. Because of the requirement that the hydrogen  $s$  band contain one electron for large Si-H separations, it will have to adjust so that the Si Fermi level lies within it. This will occur via a slight charge transfer between the H atom plane and the Si dangling-bond states so that an electrostatic potential drop will exist between them. The potential drop is, essentially, a contact potential. The plane of H atoms and the Si are two materials with different work functions, and the requirement that all one-

electron states in the system be populated according to a common Fermi distribution in effect connects a wire between them. While the maintenance of the H atoms in a single plane as they desorb is highly artificial, similar problems with the alignment partially occupied levels will occur in any theoretical study of desorption employing statistically populated one-electron states.<sup>12</sup>

Before closing our discussion of the spectral properties of the Si-H surface we consider a final surface-state band near  $-0.2$  a.u. and having the same symmetry as the bonding Si-H surface-state bands. This band which exists for the clean surface above one of the bulk bands at  $\vec{k}_{\parallel}=K$ , drops below it with H adsorption. The charge density in this state along the Si-H bonding direction is plotted in Fig. 8(c) for two Si-H separations. Notice how the H draws the charge density toward it for close Si-H separation. The change in energy with Si-H separation for this state lies somewhere between that for the bonding states of the same symmetry and the bridge states of different symmetry.

## V. IONIC CHARACTER AND WORK-FUNCTION CHANGES

In this final section we consider briefly the question of charge transfer and work-function change with H chemisorption. The effect of H chemisorption is to lower the work function of the clean surface by well over 1.0 eV. The conventional conclusion would be that there is significant charge transfer between the H and Si, in complete disagreement with what one would infer from the electronegativity difference between the Si and H. The apparent contradiction is quickly resolved when one examines the change in work function with H-Si separation. There is, in fact, essentially none. H has no effective charge—the Si-H bond is totally covalent. The induced work-function change was brought about by the promotion of one of the dangling-bond electrons to the bridge bond band. Since the latter extended considerably less into the vacuum region this causes an initial dipole change which is not, however, reflective of ionic charge transfer between the Si substrate and the H overlayer. Analogous examples illustrating the problems of relating ionic character of dipole moments in small molecules abound in the chemical literature. For example,  $\text{NH}_3$  and  $\text{NF}_3$  have dipole moments of 1.5 and 0.2 D, respectively, in spite of the fact that relative electronegativity differences between H and N and N and F are quite similar.<sup>13</sup> The resolution of the apparent inconsistency between electronegativity scales and di-

pole moment is found here in the role of the lone pair on each of the molecules, which enhances the dipole moment in the case of  $\text{NH}_3$ , and reduces it in that of  $\text{NF}_3$ . In light of the above, it

would appear that considerably greater caution should be exercised than is usually the case in relating bond lengths and ionicity differences to work-function changes.

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