

Mott insulator model of the Si(111)-(2×1) surface^{a)}

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Theoretical cluster calculations for the Si(111)-(2×1) surface lead to a description in which there is a *singly occupied* dangling bond on each surface atom. These orbitals are weakly coupled, forming a nondegenerate, nonmetallic two-dimensional Mott insulator, a description involving very strong electron correlation effects. Strong experimental support for this Mott insulator description is provided by (i) the magnitude of Si(2*p*) core level shifts, (ii) the dispersion of the dangling bond energy bands, and (iii) the absolute ionization potential from the dangling bond levels.

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I. INTRODUCTION

The Si(111) surface is one of the most studied surfaces, both experimentally¹⁻⁵ and theoretically.⁶⁻¹² For the cleaved (2×1)-Si(111) surface, a buckling model⁶⁻¹³ for the reconstruction has been widely used in the interpretation of results.⁶⁻¹⁵ Recently, an increasing amount of experimental evidence^{5,16,17} has indicated difficulties with this buckling model of the (2×1)-Si(111) reconstruction.

In the present paper we report the results of fully correlated theoretical calculations using cluster models and we compare these results with three major experiments: (i) the Si(2*p*) core level shifts,^{14,15} (ii) the dispersion of the dangling bond surface states,^{5,16} and (iii) the (angle-integrated) ionization potential (IP) from the dangling bond orbitals.¹⁸ These comparisons show that on the surface there are very strong *electron correlation effects* that lead to *singly occupied* dangling bond orbitals¹⁹ (one per surface atom). The ground state of the surface is of the form of a nondegenerate, nonmetallic *Mott insulator*.¹⁶

Using this Mott insulator model for the ground state of the surface, we carried out theoretical calculations for the dangling bond energy dispersions along the main symmetry lines of the surface Brillouin zone (SBZ). Fully correlated, self-consistent wave functions [generalized valence bond (GVB) and configuration interaction (CI)] as well as the closed-shell Hartree-Fock (HF) wave function were used. Comparison between the correlated and uncorrelated calculations and the experimental results of Himpsel *et al.*^{5,16} shows that electron correlation effects are of crucial importance, leading to surface atoms having singly occupied dangling bond orbitals.

The calculated IP is in excellent agreement with the experimental (angle-integrated) IP.¹⁸

We also calculated the Si(2*p*) core level shifts (including spin-orbit coupling) for surface atoms of Si(111). The resulting Si(2*p*) core level shifts are in good agreement with experiment,^{14,15} even though our calculations treat all surface atoms as equivalent (no buckling). These results argue strongly against the charge-transfer model^{6-8,20} often used to describe the electronic structure of the surface.

We also report the results of geometry optimizations (based on total energy minimization) for Si₄H₉ and Si₉H₁₅

clusters that indicate that nearest-neighbor interactions lead only to relaxation of the surface atoms (no buckling). This indicates that geometric rearrangements of the surface atoms responsible for the experimentally observed 2×1 reconstruction are probably due to cooperative interactions involving a large number of atoms.

II. RESULTS AND DISCUSSION

A. Geometry optimizations

For the symmetric (1×1) relaxation we obtained the results shown in Table I. For cluster (c) in Fig. 1, we find an optimum relaxation of $d_{\perp} = -0.14$ Å (toward the bulk, with respect to the tetrahedral geometry), in excellent agreement with the value of $d_{\perp} = -0.16$ Å obtained recently from dynamic LEED studies²¹ on Te-stabilized Si(111)-(1×1). The energy associated with this relaxation is quite small (0.055 eV ≈ 1 kcal/mol).

Calculations were carried out on cluster 1(c) in which alternate surface atoms were displaced up and down relative to the relaxed 1×1 geometry. In all cases we found the symmetric geometry to be most stable. We also investigated the possibility of a non-C_{3v} symmetry environment for the surface Si atoms. To this effect, calculations were performed on

TABLE I. Geometric relaxation of Si clusters [Si(111)-(1×1)].

	d_{\perp} ^{a)} (Å)	ΔE_{relax} (eV)	
Neutral	Si ₄ H ₉	-0.122	0.042 ^{b)}
	Si ₉ H ₁₅	-0.144	0.055 ^{b)}
Positive ion	Si ₄ H ₉	-0.494	0.114 ^{c)}
Negative ion	Si ₄ H ₉	+0.137	0.140 ^{c)}

^{a)} Optimum position of the relaxed surface Si referenced with respect to the value for the tetrahedral bulk terminated position; positive is away from the surface.

^{b)} Energy of tetrahedral structure relative to optimum structure.

^{c)} Relative to structure with $d_{\perp} = -0.12$ Å.

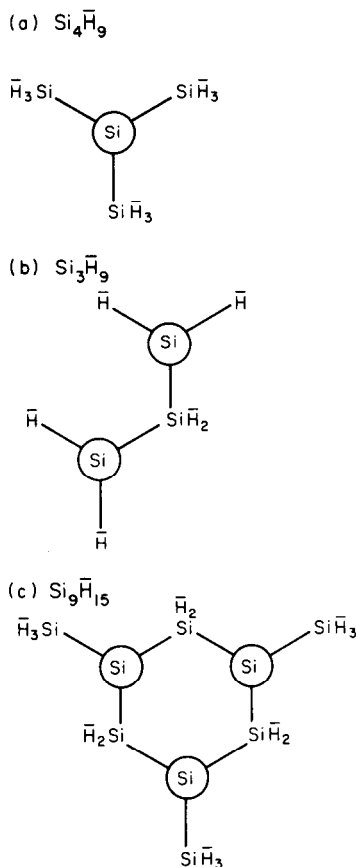


FIG 1. Clusters used in various calculations (see text). Large circles denote surface atoms.

clusters 1(a) and 1(c) where the surface atoms were allowed to move laterally, permitting two adjacent surface silicons to come closer together, thus giving a 2×1 structure. Again, we found that the relaxed 1×1 geometry was the most stable one. We also performed calculations on cluster 1(c) in which a wave function with singly occupied, singlet-coupled dangling bonds was allowed to resonate²² (with nonzero overlap) with a charge transfer (zwitterion) type of wave function. Again, we found that the symmetric relaxed (1×1) geometry had the lowest energy.

All of these calculations lead to the conclusion that the mechanism responsible for the reconstruction is not due to nearest-neighbor interactions. Hence, such reconstruction probably results from collective interactions in which large numbers of surface and subsurface atoms are involved.

B. Ionization potentials

In Table II we show the IP's and electron affinities for different relaxation distances, as calculated for the $\text{Si}_4\bar{\text{H}}_9$ cluster [Fig. 1(a)]. At the optimum geometry for the neutral system, we calculate an IP from the dangling bond orbital of 5.71 eV. Using a value of 5.15 eV for the position of the top of the valence band,¹⁸ this result corresponds to a surface dangling bond state bound by 0.6 eV with respect to the valence band minimum (VBM). This is in excellent agreement with the experimental results (IP = 5.6 to 5.9 eV),¹⁸ providing evidence in favor of the surface orbitals being singly occupied dangling bond orbitals.

TABLE II. Ionization potential and electron affinity of dangling bond orbital.

Cluster	d_1 (Å)	IP (eV)		EA ^{c)} (eV)
		Theory ^{a)}	Experiment ^{b)}	Theory
$\text{Si}_4\bar{\text{H}}_9$	0	5.999		1.752
	-0.14	5.711	5.6-5.9	1.609
	-0.28	5.448		1.522
	-0.40	5.259		1.482
	Adiabatic	5.390		1.749

^{a)} Relative to vacuum, subtract 5.15 eV to obtain the surface IP relative to the VBM.

^{b)} Reference 18.

^{c)} Since the negative ion state was not correlated, and since no diffuse basis functions or d basis functions were included, these values for EA should be low by 1 to 2 eV.

C. Si(2p) core levels

Because of changes in the effective charge at the surface atoms, it is expected that there will be a chemical shift of the Si(2p) core of IP's of the surface atoms relative to the bulk atoms. Thus, for a structure such as Si(111)-(2 × 1), one expects two inequivalent surface atoms and hence two different surface Si(2p) levels. Indeed, experiments by Brennan *et al.*¹⁵ were interpreted in terms of two surface levels shifted by $+0.30 \pm 0.03$ eV and -0.59 ± 0.04 eV with respect to bulk levels (their reference for the bulk value was obtained by oxidizing the surface). They interpreted these two levels as derived from the inward Si (+0.30 eV) and outward Si (-0.59 eV) of the pairing model¹³ of the (2 × 1)-Si(111) surface. Similarly, Himpsel *et al.*¹⁴ found three surface levels at -0.37, -0.14, and +0.16 eV (the reference for the bulk value was obtained by hydrogenating the surface). They tentatively assigned the -0.37 eV feature to the raised atom and one of the other two features to the inward atom of the pairing model.

In order to explore these effects, we carried out two sets of calculations. First, using the $\text{Si}_4\bar{\text{H}}_9$ cluster [Fig. 1(a)] we considered the core ionization at a single Si atom, as indicated in Table III. Even a single surface Si atom leads to four different Si(2p) core level ionizations (ignoring spin-orbit coupling). The reasons are, first, that the chemical environment at the surface Si is anisotropic, so that an Si 2pσ level [Si(2p) hole perpendicular to the surface] has an energy different from an Si 2pπ level [Si(2p) hole parallel to the surface]. Secondly, the dangling bond orbital on the surface Si can be paired with either type of Si(2p) hole to form both triplet and singlet states. Thus (ignoring spin-orbit coupling), we end up with four Si(2p) levels: $^1\sigma$; $^1\pi$; $^3\pi$; and $^3\sigma$, in order of decreasing IP (see Fig. 2 and Table III).

When we include the spin-orbit interaction, these four levels split up into eight levels: $^1\sigma_0(1)$ at +0.34; $^1\pi_1(2)$ at +0.23; $^3\pi_{0-}(1)$ at +0.18; $^3\pi_{0+}(1)$ at -0.24; $^3\pi_1(2)$ at -0.33; $^3\pi_2(2)$ at -0.38; $^3\sigma_1(2)$ at -0.52; and $^3\sigma_0(1)$ at -0.53 eV (weights are given in parentheses). These values are calculated for cluster 1(a) relative to the bulk calculated value²³ of 105.39 eV. The three levels with positive core shifts ($^1\sigma_0$, $^1\pi_1$, and $^3\pi_{0-}$) are associated with the bulk $2p_{1/2}$ state, while the other five states are associated with the bulk

TABLE III. Silicon ($2p$) core levels IP's (in eV) for the surface Si of the $\text{Si}_4\bar{\text{H}}_6$ cluster as a function of surface relaxation (d_1). The calculated IP for the bulk Si model is^{a)} 105.39 eV. The IP's for the surface Si are with respect to this value (positive means higher IP; weights are in parentheses).

State	d_1 (Å)			
	0.00	-0.14	-0.28	-0.40
(a) No spin-orbit coupling				
$^1\sigma$ (1)	+0.29	+0.07	-0.07	-0.13
$^1\pi$ (2)	+0.20	-0.07	-0.09	-0.09
$^3\pi$ (6)	+0.05	-0.17	-0.19	-0.17
$^3\sigma$ (3)	-0.30	-0.39	-0.41	-0.41
(b) With spin-orbit coupling ^{b)}				
$^1\sigma_0$ (1)	+0.56	+0.34	+0.26	+0.25
$^1\pi_1$ (2)	+0.45	+0.23	+0.20	+0.21
$^3\pi_0$ (1)	+0.38	+0.18	+0.16	+0.17
$^3\pi_0$ (1)	-0.01	-0.24	-0.32	-0.35
$^3\pi_1$ (2)	-0.08	-0.33	-0.35	-0.34
$^3\pi_2$ (2)	-0.15	-0.38	-0.39	-0.38
$^3\sigma_1$ (2)	-0.41	-0.52	-0.55	-0.54
$^3\sigma_0$ (1)	-0.42	-0.53	-0.56	-0.55
W_π ^{c)}	0.60	0.59	0.59	0.59
W_σ	0.98	0.87	0.82	0.80
$W_{p_{1/2}}$	0.18	0.16	0.10	0.08
$W_{p_{3/2}}$	0.41	0.31	0.24	0.20

a) Reference 23.

b) Using $\lambda = -0.41$ eV from Ref. 14.

c) W_i indicates the total range of IP for states associated with character i .

$2p_{3/2}$ level.

These calculations show that the widths of the bulk-derived $2p_{1/2}$ and $2p_{3/2}$ peaks should not be taken as equal (contrary to previous assumptions^{14,15}) in the interpretation of the experimental data.

The total splitting between the $2p_{3/2}$ derived levels of 0.3 eV is in reasonable agreement with the experimental result of

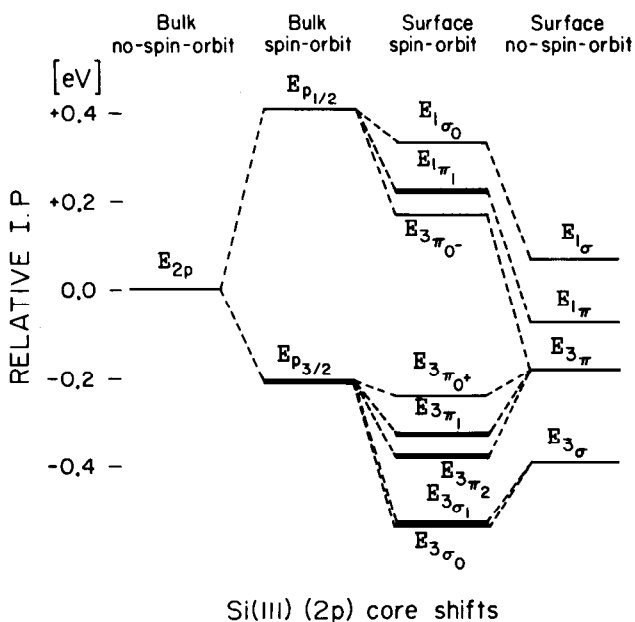


FIG 2. Calculated Si($2p$) core level shifts. Thick lines denote doubly degenerate states.

0.53 eV of Himpsel *et al.*¹⁴ The total splitting between the $^1\sigma_0$ and $^3\sigma_0$ states is 0.9 eV (for the relaxed optimum geometry), which is in good agreement with experimental results by Brennan *et al.*¹⁵ who obtain a width of ~ 0.9 eV.²⁴ Thus, the core level shifts are consistent with no buckling of the Si(111)-(2 \times 1) surface. A good experimental test of our predictions would be to study the surface core level intensities as a function of photon polarization. We predict that the largest splitting (0.9 eV) is for the $2p\sigma$ ionization (favored by having the polarization direction perpendicular to the surface, e.g., a grazing incidence), while the smallest splitting (0.6 eV) is for $2p\pi$ ionization (favored by having polarization parallel to the surface, e.g., normal photon beam).

In order to determine how buckling of the surface would affect the core level shifts, we used an $\text{Si}_3\bar{\text{H}}_6$ cluster [Fig. 1(b)] to examine the core levels for two geometries: (i) a buckling of 0.30 Å (Feder *et al.*²⁵), and (ii) a buckling of 0.75 Å (Chadi²⁰). As indicated in Table IV, a buckling of 0.3 Å leads to additional shifts of between 0.24 and 0.29 eV between corresponding levels on the two Si atoms, whereas a buckling of 0.75 Å leads to additional shifts of between 0.49 and 0.83 eV. Note that the *outer surface* Si atom has a *larger* IP than the inner one, as expected from the results for the $\text{Si}_4\bar{\text{H}}_6$ cluster (Table III). This is opposite to the usual assumption and results from electronic relaxation in the final (ion) state.

The Si(111)-(2 \times 1) surface has often been described in terms of a charge transfer, so that the dangling bond orbital is doubly occupied for the outer Si and empty for the inner atom. Indeed, we find that closed-shell HF calculations yield just this sort of wave function¹⁹ [correlating the electrons leads to a lower energy (2.7 eV per pair) and one singly occupied dangling bond orbital on each surface Si]. In order to compare with the results obtained from wave functions with doubly occupied surface orbitals, we have evaluated the Si($2p$) core level energies (Table IV) for an *ab initio* closed-shell HF calculation. For both the 0.3 and 0.75 Å buckling cases we find that the Si($2p$) core level IP for the outer Si is 2.3 to 2.6 eV lower than that of the inner Si. The fact that the experimental range is 0.5–1.2 eV provides a strong argument against the use of such wave functions to describe the dangling bond states of Si(111).

D. Energy dispersion curves for dangling bond states

Consider the ground state of the surface, consisting of a singly occupied dangling bond orbital on each surface Si singlet-spin-paired to another such orbital, as shown schematically in Fig. 3. This leads to a nondegenerate, nonmetallic ground state (a two-dimensional Mott insulator.) For the $\text{Si}_9\bar{\text{H}}_{15}$ cluster [Fig. 1(a)] we calculate an excitation energy of 0.88 eV for the first excited state. This corresponds to an upper bound for the optical gap in a band calculation. The observed optical gap is ~ 0.45 eV.²⁶

To compare with photoemission spectra, we must consider the final positive ion states obtained by removing an electron out of the ground state of the surface. Suppose that the electron being removed comes out of the pair denoted by the orbitals ϕ_l and ϕ_r in Fig. 3. There are two possible positive-ion final states. One consists of an electron whose orbital has

TABLE IV. Effect of buckling on surface core level shifts [from cluster 1(b); all energies in eV].

		Geometry 1			Geometry 2		
Relaxation (Å)		- 0.08			- 0.065		
Buckling (Å)		0.30			0.75		
		Up-down splitting ^{a)}					
		GVB ^{b)}	KT-GS ^{c)}	KT-HF ^{d)}	GVB ^{b)}	KT-GS ^{c)}	KT-HF ^{d)}
π		0.26	0.30	- 2.29	0.60	0.78	- 2.56
		0.24	0.31	- 2.32	0.49	0.79	- 2.58
σ		0.29	0.32	- 2.34	0.83	0.83	- 2.59
		Absolute IP (up atom)					
π		105.67	115.92	114.81	105.98	116.33	114.94
		105.67	115.92	114.80	105.84	116.32	114.93
σ		105.32	115.89	114.75	105.79	116.32	114.89

^{a)} Difference between same state on up atom and on down atom; for SCF calculations, down atom is easier to ionize.

^{b)} Selfconsistent GVB calculation; IP obtained by subtracting the energy of the ground state from that of the positive ion.

^{c)} Koopmans' theorem IP using correlated ground state wave function.

^{d)} Koopmans' theorem IP using HF closed-shell wave function.

the form of a symmetric combination ($\phi_l + \phi_r$) of the original dangling bond orbitals. The other final state corresponds to the antisymmetric combination ($\phi_l - \phi_r$). These two final states lead to two different energy dispersion relationships for the singly occupied final state dangling bond orbitals, given by [assuming all surface atoms are equivalent and including only nearest (surface) neighbor interactions]:

$$E_{l+r}(\mathbf{k}) = \alpha - 2\beta \cos(2k_x a) - 6\beta \cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) - 2\beta \cos\left(\frac{3k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right), \quad (1)$$

and

$$E_{l-r}(\mathbf{k}) = \alpha + 2\beta \cos(2k_x a) - 2\beta \cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) + 2\beta \cos\left(\frac{3k_x a}{2} - \frac{\sqrt{3}k_y a}{2}\right), \quad (2)$$

where $\alpha = -0.90$ eV and $\beta = 0.078$ eV are the parameters

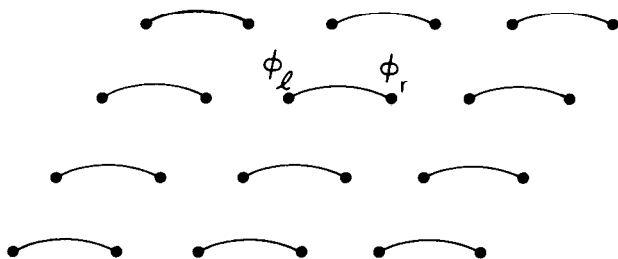


FIG 3. Mott insulator model of the surface ground state. Only surface atoms are shown. Each surface atom is considered to have a singly occupied dangling bond orbital that is singlet-paired to that on an adjacent center (pairing indicated by a solid line).

in the two-dimensional band calculation ($a = 3.84$ Å), obtained from CI calculations for the positive ions of the $\text{Si}_9\bar{\text{H}}_{15}$ cluster. [Similar expressions for 2×1 buckled surfaces involve a total of eight α 's and β 's even for just nearest (surface) neighbor interactions. However, we find that the hopping (β) parameters depend only weakly upon buckling (for buckling ≤ 0.3 Å). Consequently, the results of Fig. 3(b) also apply to slightly buckled surfaces.] These two dispersion relationships are plotted in Fig. 4(b) and compared with experimental results by Himpsel and Eastman^{5,16} in Fig. 4(a). The most valid comparison of the theoretical and experimental curves requires use of the transition probabilities at different points in the surface Brillouin zone for the two different final positive-ion states. We have not calculated these matrix elements; however, some considerations are possible: (i) for the $\bar{\Gamma}$ point the transition moment for $l-r$ is zero so that only one band should be observed, and (ii) regions of little dispersion lead to high density of states and should tend to dominate the photoemission spectra. As expected from the theory, there is only one band observed near $\bar{\Gamma}$ but two observed near \bar{J} . Assuming that the $l+r$ band would have the largest matrix elements, we interpret the Himpsel-Eastman experiments as indicated in Fig. 4(a), leading to an experimental dispersion of -0.56 eV in the $\phi_l + \phi_r$ band. We calculate a dispersion of -1.28 eV in this band; however, these calculations consider only nearest-neighbor effects. At \bar{J} , the experimental separation of the $\phi_l + \phi_r$ and $\phi_l - \phi_r$ bands is -0.46 eV, which is in reasonable agreement with the theoretical value of -0.31 eV. Overall, the agreement between experiment and theory is good, providing experimental support for the notion that the $\text{Si}(111)-(2 \times 1)$ surface has singly occupied dangling bond orbitals and little distortion of the surface atoms.

In order to provide a theoretical comparison with the charge transfer model of the surface, we also calculated the

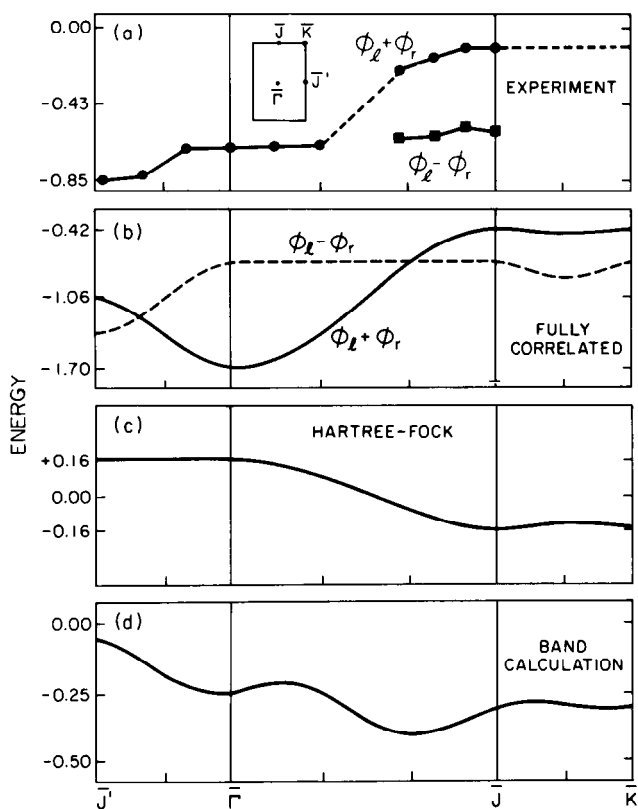


FIG 4. Experimental (Ref. 5) and calculated energy band dispersions for surface states on Si(111)-(2 \times 1). The calculated bands in (b) and (c) use parameters obtained from *ab initio* cluster calculations. The band calculation in (d) is from Ref. 6. All energies are in eV, referenced to the VBM.

surface band dispersions for a closed-shell HF wavefunction (the normal type of band description of the surface) using parameters obtained from *ab initio* calculations on clusters. Using only nearest-neighbor interactions leads to a surface band dispersion of

$$E^{\text{HF}}(\mathbf{k}) = \alpha^{\text{HF}} - 2\beta^{\text{HF}} \cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right), \quad (3)$$

with $\alpha^{\text{HF}} = -0.01$ eV and $\beta^{\text{HF}} = 0.144$ eV. These results are shown in Fig. 4(c) where we see that (i) the dispersion is opposite that of the experiments, and (ii) there is only one band. Thus, the experimental results argue strongly against the use of the simple HF band description of the surface.

Also included in Fig. 4(d) is the surface band dispersion obtained by Pandey and Phillips⁶ from more complete band calculations. These results are also in strong disagreement with experiment.

E. Implications for the Si(111)-(1 \times 1) surfaces

The (2 \times 1) pairing of orbitals indicated in Fig. 3 is the simplest such pairing. Note in particular here that each pair of atoms connected by a bonding line is singlet-paired so that there is not net spin density on either atom.

One can also imagine a case in which all surface atoms are paired as in Fig. 3 but with no long-range order on how adjacent pairs are coupled. In this case one would not observe the half-order LEED spots characteristic of the (2 \times 1) structure and the LEED patterns would appear as (1 \times 1).

Indeed, the (1 \times 1) structures obtained by laser annealing or by impurity stabilization could have just this form of a disordered version of Fig. 3. If so, the core level IP's should be exactly the same as for the 2 \times 1 surface. We suggest that this experimental test be performed.

F. Comparison with other theoretical studies

All previous theoretical treatments of the Si(111) surface have utilized closed-shell HF wave functions leading, we believe, to a totally incorrect description of the surface. However, at this same AVS meeting, Chadi²⁷ and Duke²⁸ have both suggested using the Hubbard Hamiltonian to describe the Si(111) surface. The Hubbard Hamiltonian corresponds to a semiempirical GVB wave function in which a fictitious one-center, two-electron integral U is added to discourage the presence of doubly occupied orbitals.

Chadi's description²⁷ is in the framework of unrestricted HF (UHF) theory, so that half the atoms have up spin and half have down spin. We believe that this apparent antiferromagnetic behavior is just an artifact of the use of the single-determinant UHF wave function. In our wave function each electron is spin-paired to an adjacent one, leading to an overall singlet ground state and no net spin density on the surface atoms.

Duke suggested²⁸ that the laser annealed 1 \times 1 structures have the form of singlet-paired dangling bond orbitals on adjacent centers but without long-range order.

III. CALCULATIONAL DETAILS

We considered the three finite clusters indicated in Fig. 1, where H atoms are used to terminate what would have been Si-Si bonds of solid Si. Using an Si₅H₁₂ cluster to model bulk Si, we required that the H atoms be such that the central Si has a neutral charge when the H is placed at the usual Si position. The resulting $\bar{\text{H}}$ atoms (referred to as *siligen* atoms) correspond to Slater-type orbitals with a scale factor of $\zeta = 0.2944$, a value that leads to $\bar{\text{H}}$ having an electronegativity corresponding to bulk Si.²³

Clusters 1(a) and 1(c) were used to calculate symmetric distortions (i.e., 1 \times 1) of the surface Si atoms. The surface atoms were constrained to move perpendicular to the surface, $\bar{\text{H}}$ atoms representing surface Si atoms were moved as if they had been real Si atoms, and second-layer Si atoms and $\bar{\text{H}}$ representing third-layer Si's were kept fixed. Clusters 1(b) and 1(c) were used to investigate asymmetric distortions (pairing model²³) of the surface Si atoms. Cluster 1(a) was also used to investigate the possible geometries having local C_s symmetry about the surface Si.

The electrons involved in surface orbitals [one for 1(a), two for 1(b), and three for 1(c)] were fully correlated and all possible spin states were calculated [$S = \frac{1}{2}$ for 1(a), $S = 0, 1$ for 1(b), and $S = \frac{3}{2}, \frac{1}{2}$ for 1(c)]. In addition, for 1(b) we solved for the traditional closed-shell HF wave function.

For cluster 1(a), the positive and negative ion states were calculated self-consistently as a function of relaxation of the surface Si. For cluster 1(c), the various ion states ($S = 0, 1$) of the surface were also calculated self-consistently. From these calculations we evaluated the coupling elements between surface orbitals that were used to calculate the dan-

gling bond dispersion relationships for the surface states.

For clusters 1(a) and 1(b) we solved self-consistently for the states in which a single Si($2p$) core level was ionized. Here we solved for the $^3\sigma$, $^3\pi$, $^1\pi$, and $^1\sigma$ states (no spin-orbit coupling) of the core positive ion. Although a considerable amount of care has to be taken to obtain initial trial functions for these states, the final results correspond to completely self-consistent wave functions. In order to include the effect of the spin-orbit interaction, we diagonalize the spin-orbit Hamiltonian in the full space of the SCF states.

In addition, we calculated the core levels using ground state wavefunctions plus Koopmans' theorem. From Table IV we see that use of Koopmans' theorem leads to core-level IP's 10 eV larger than those calculated self-consistently. This difference represents the final-state shielding of the core-level hole obtained in the self-consistent calculation. Because of this large effect, we feel that use of Koopmans' theorem is invalid for describing core-level ionizations.

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