

# Electronic correlation and the Si(100) surface: Buckling versus nonbuckling

Antonio Redondo and William A. Goddard III

Arthur Amos Noyes Laboratory of Chemical Physics,<sup>a)</sup> California Institute of Technology, Pasadena, California 91125

(Received 27 January 1982; accepted 22 April 1982)

Theoretical cluster calculations for the Si(100) surface show that the use of doubly occupied orbital wavefunctions, such as the closed-shell Hartree-Fock (HF), lead to an asymmetric dimer description of the surface. The inclusion of electron correlation produces a symmetric dimer description with a ground state  $\sim 1.0$  eV below the minimum of the HF buckled dimer. There are two low-lying states of the symmetric dimer (a singlet and a triplet) with very different geometries. Energy minimization calculations indicate that a  $(2 \times 1)$  structure is favored over a  $c(2 \times 2)$  structure. We also report ionization potentials for surface and Si(2*p*) core electrons that are consistent with current experimental data.

PACS numbers: 73.20.Cw, 68.20. + t

## I. INTRODUCTION

Although the Si(100) surface is commonly used in device applications, there continue to be numerous uncertainties concerning the character of the bare surface and of the oxide interfaces with this surface.

The unreconstructed Si(100) surface consists of divalent Si atoms, each bonded to two subsurface silicons. These surface atoms are second-nearest neighbors for the bulk crystal, but it is commonly accepted that each surface atom is displaced about  $0.75 \text{ \AA}$  so as to make a covalent bond to one other surface atom. This is referred to as the dimer or pairing model.<sup>1-5</sup> The issues concerning the states of the bare surface are (i) Is the basic paired unit distorted (asymmetric dimer) or are both surface Si equivalent (symmetric dimer)? (ii) How are the different dimers ordered with respect to each other; thus, is the overall structure  $(2 \times 1)$ ,  $c(2 \times 2)$ ,  $p(2 \times 2)$ ,  $c(4 \times 2)$ ?

Experimental studies<sup>6</sup> using LEED suggest that the basic structure is  $2 \times 1$ ; however, the studies by Poppendick *et al.*<sup>7</sup> on samples that were annealed at high temperature indicate a  $c(4 \times 2)$  structure. In neither case has analysis of the intensity versus energy curves led to reliable positions for the atoms.

Photoelectron studies<sup>8</sup> show the presence of two surface bands separated by 0.5 eV, and angle-resolved studies<sup>8</sup> have mapped out the dispersion in these surface bands. In addition, the chemical shifts in the Si(2*p*) core levels of surface atoms have been determined.<sup>9</sup>

Semiempirical total energy calculations<sup>4</sup> based on Hartree-Fock (HF) lead to an asymmetric dimer with a relative vertical displacement (buckling) of 0.45 to 0.65  $\text{\AA}$  for the surface atoms. This model has been used to rationalize<sup>1-6,10</sup> the  $p(2 \times 1)$ ,  $c(2 \times 2)$ , and  $c(4 \times 2)$  structures and the dispersion in the surface dangling bond levels.

Herein we report *ab initio* calculations on finite cluster models of the Si(100) surface. These calculations include the dominant electron correlation effects [generalized valence bond (GVB), configuration interaction (CI)] and lead directly to total energies that can be used to calculate optimum surface geometries. We find that electron correlation effects play a dominant role. While uncorrelated HF calculations

lead to large distortions in the geometry, correlated calculations lead to a symmetric dimer.

We report results relating to (i) the geometry of the surface dimers (the Si-Si bond is stretched; the dimer is symmetric); (ii) the electronic states of the dimer (the ground state has the two nonbonded dangling bond orbitals paired into a singlet state; the triplet pairing is very low-lying but has a much larger Si-Si distance); (iii) the coupling between surface dimers induced by the subsurface atoms [ $2 \times 1$  distortions are favored over  $c(2 \times 2)$  distortions]; (iv) the energy splitting and dispersion of the dangling bond surface bands (we find two bands of states corresponding to the dangling bonds, separated by 0.5 eV, plus a surface band corresponding to the Si-Si bond of the dimer, 1.3 eV lower); and (v) the Si(2*p*) core ionization spectrum [we find that coupling of the surface valence levels leads to four groups of Si(2*p*) levels spread over a total width of 1.2 eV].

These new theoretical results are consistent with the experimental data but suggest some new experiments that could provide a strong test of these predictions.

## II. CALCULATIONAL DETAILS

The present methods have been used for a number of studies<sup>11</sup> on Si(111) surface models. We use an *ab initio* effective potential<sup>12</sup> to replace the core electrons of Si, except when calculating core levels. All valence electrons are solved for self-consistently using *ab initio* methods (evaluation of all one- and two-electron integrals) including electron correlation (many-body effects) in the electrons of the surface atoms. Electron correlation is included by using the GVB<sup>13</sup> and CI<sup>13</sup> methods.

In calculations of the core levels, we have solved for the final states self-consistently, including all valence electrons in the surface atoms. Thus, all relaxation effects are included (final state relaxation is 10–15 eV and *must* be included for reliable results<sup>11</sup>).

The model used for these calculations is indicated in Fig. 1. This cluster has nine Si atoms plus 12 hydrogens, which are used to terminate the cluster.<sup>11,14</sup> For the terminating hydrogen atoms, we use siligens<sup>11</sup> centered at the corre-

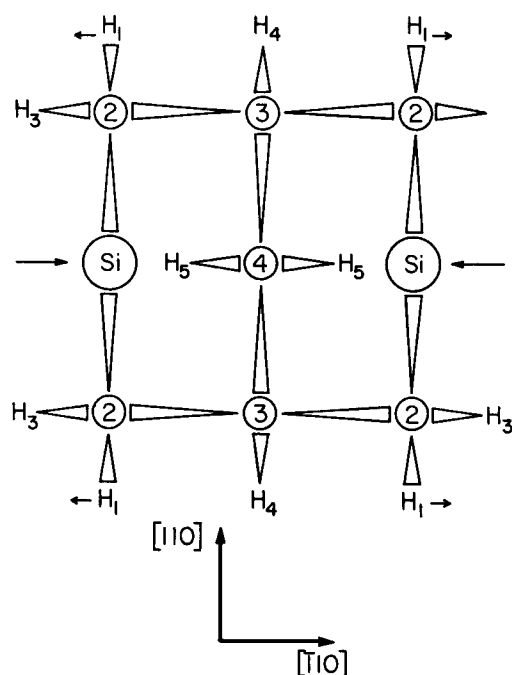


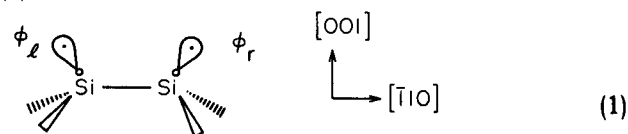
FIG. 1.  $\text{Si}_7\text{H}_{12}$  model of the  $\text{Si}(100)$  surface. Large circles indicate the two surface Si atoms. The other seven silicon atoms are denoted by small circles with numbers indicating the layer to which they belong. Hydrogens are indicated by  $\text{H}_i$ , where  $i$  is the layer position. Arrows on the surface atoms indicate the distortions considered.

sponding Si positions and having properties adjusted to mimic bulk silicon. In considering distortions of the surface silicons as the bond is formed, we also move the siligens by corresponding amounts, as indicated in Fig. 1.

### III. GEOMETRIC AND ELECTRONIC STRUCTURE

#### A. GVB description

After forming a single bond between two surface atoms, we are left with a dangling bond orbital on each surface Si, as in (1),



These two dangling bond orbitals  $\phi_l$  and  $\phi_r$  can be paired into two states: a singlet state<sup>15</sup>

$$\Psi_s(1,2) = [\phi_l(1)\phi_r(2) + \phi_r(1)\phi_l(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (2)$$

and a triplet state<sup>15</sup>

$$\Psi_T(1,2) = [\phi_l(1)\phi_r(2) - \phi_r(1)\phi_l(2)] \times \begin{cases} [\alpha(1)\alpha(2)] \\ [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ [\beta(1)\beta(2)] \end{cases} \quad (3)$$

[the other 46 valence electrons of our cluster have been ignored here for simplicity; all these orbitals plus those of the surface electrons are calculated self-consistently].

The calculated orbitals for the singlet and triplet states are shown in Fig. 2. In this figure, each orbital has one electron and has been calculated using the GVB method. We see that the  $\phi_l$  and  $\phi_r$  orbitals are  $s-p$  hybrids with a fair amount of  $p$  character. To whatever extent the  $\phi_l$  and  $\phi_r$  orbitals overlap, the singlet state will lead to additional bonding, whereas the triplet state will lead to antibonding. Thus, the singlet state should have a shorter Si-Si bond length than the triplet state. For carbon systems, the  $\phi_l-\phi_r$  bond for the singlet state

Si (100) dangling bond and Si-Si bond orbitals

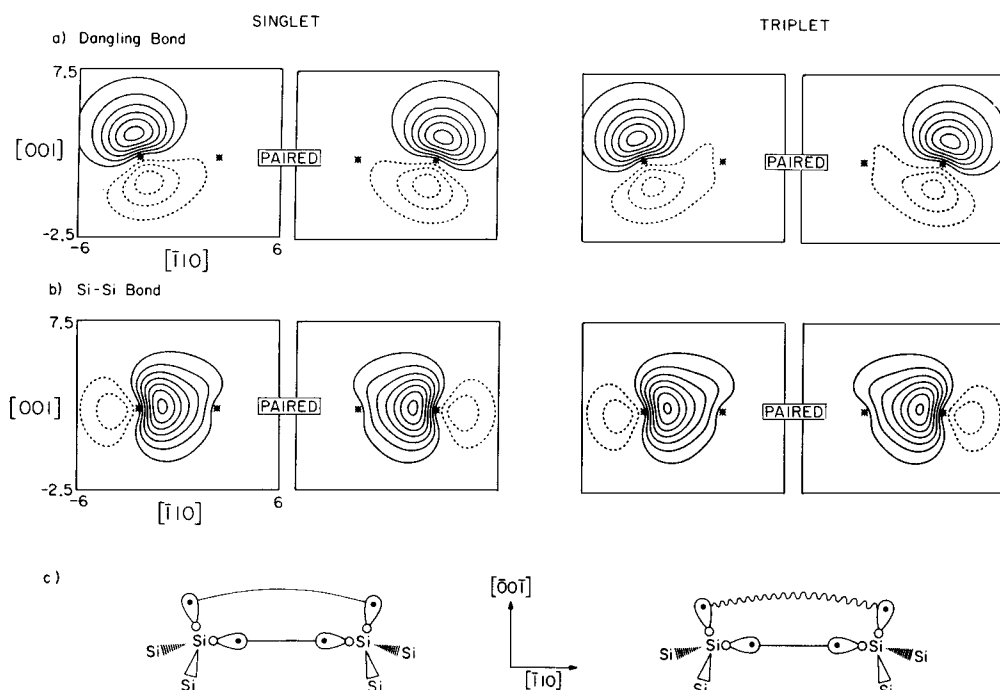


FIG. 2. Amplitude plots for the surface orbitals for the GVB calculated singlet and triplet states of the symmetric dimer (at the singlet geometry). Solid lines indicate positive amplitudes; dashed lines indicate negative amplitudes. Surface atoms are indicated by asterisks. Distances are in bohr atomic units. The contours are plotted every 0.03 a.u. (a) Dangling bond orbitals; (b) dimer Si-Si bond orbitals; (c) schematic for the electronic structure. A smooth line between two orbitals indicates singlet coupling; a wiggly line indicates triplet pairing; dots indicate the number of electrons.

TABLE I. Optimum geometries and energies for the symmetric dimer  $\text{Si}_2\bar{\text{H}}_{12}$  cluster model of the Si(100) surface. (All distances in Å and all energies in eV.)

	Singlet geometry	Triplet geometry
$d_{\text{SiSi}}^{00}$	2.47	2.66
$d_{\text{SiSi}}^{01}$	2.37	2.37
States		
Singlet <sup>(a)</sup>	0.00	0.06
Triplet <sup>(a)</sup>	0.16	0.03

<sup>a)</sup> CI calculation using the GVB singlet orbitals (see Ref. 13).

would be quite strong<sup>16</sup>; however, silicon makes weak  $\pi$  bonds, and the extra bonding in the Si(100) surface dimer is expected to be weak.

For both states, we optimized both the surface–surface bond length of the dimer (denoted as  $d_{\text{SiSi}}^{00}$ ) and the bond length between the surface and subsurface atoms (denoted as  $d_{\text{SiSi}}^{01}$ ). We find that both states lead to (see Table I),

$$d_{\text{SiSi}}^{01} = 2.37 \text{ \AA},$$

a value that is only slightly longer than the bond distance of bulk Si, 2.35 Å. On the other hand, the surface bond lengths are quite different for the two states, with

$$d_{\text{SiSi}}^{00,S} = 2.47 \text{ \AA}, \quad \text{for the singlet}$$

and

$$d_{\text{SiSi}}^{00,T} = 2.66 \text{ \AA}, \quad \text{for the triplet.}$$

This difference reflects the expected extra bonding for the singlet state.

For longer distances, the orbital overlap becomes quite small and the triplet state is favored by the electron exchange interactions. The result is a singlet ground state but a triplet state only 0.03 eV higher! The potential curves for these states are shown in Fig. 3.

So far, we have considered symmetric distortions of the pair of surface Si atoms. We have also considered asymme-

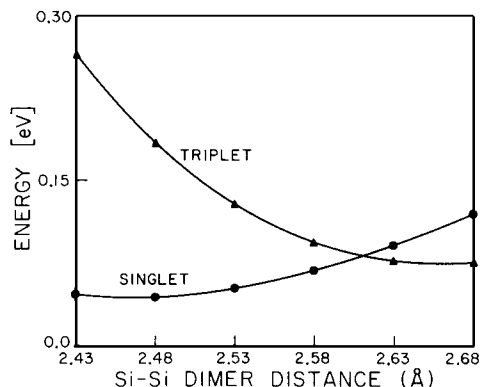


FIG. 3. Potential curves for the energy of the singlet and triplet states (GVB-CI calculation) as a function of the dimer Si-Si bond length.

tric distortions in the form of buckling, in which one surface atom moves away from the surface while the other moves toward the surface.

In calculating the effect of buckling, we kept all Si-Si bond lengths fixed and changed only the angles. The results are shown in Fig. 4 where the abscissa is the  $z$  component of the relative distance of the surface atoms (zero for the symmetric dimer). We find that both singlet and triplet states prefer an unbuckled surface.

## B. HF description

In the HF description, the two dangling bond electrons are placed in the same orbital, leading to the wave function<sup>15</sup>

$$\Psi_S^{\text{HF}} = \phi_{\text{MO}}(1)\phi_{\text{MO}}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (4)$$

[where the orbitals for the other 46 electrons have been omitted for simplicity]. The resulting self-consistent surface molecular orbital (MO) is shown in Fig. 5(a), with a shape close to the form

$$\phi_{\text{MO}} = (\phi_l + \phi_r). \quad (5)$$

Expanding the spatial part of Eq. (4), using Eq. (5), leads to the terms

$$\psi^{\text{MO}}(1,2) = \underbrace{[\phi_l(1)\phi_l(2) + \phi_r(1)\phi_r(2)]}_{\text{ionic}} + \underbrace{[\phi_l(1)\phi_r(2) + \phi_r(1)\phi_l(2)]}_{\text{covalent}} \quad (6)$$

with equal amounts of ionic and covalent character. Since the best description is with one electron in each dangling bond orbital, the MO wave function has a higher energy. One says that the motion of the two electrons in the  $\phi_{\text{MO}}$  orbital is not correlated. On the other hand, the GVB wave functions has one electron in each orbital so that the electronic motion is correlated.

This results in a calculated HF energy 1.33 eV higher than the GVB energy. However, the HF description of the triplet state leads to orbitals just as in Eq. (3). This leads to no artificial ionic terms and, consequently, in the HF description, the triplet state is 1.33 eV lower than the singlet! Thus, *the HF description of the entire surface* leads to triplet states for each Si pair which would be weakly coupled to produce a *ferromagnetic ground state!*

Now consider the buckling distortions of the surface dimer. For a distorted surface the HF orbital is expected to localize on the outer Si, leading to a description of the form



In turn, the surface Si-Si bond will polarize to shield the positive charge on the inner Si. The result is a neutral charge distribution with less ionic character than in the symmetric dimer [Eq. (6)]. Consequently, the energy of the HF singlet state decreases for the asymmetric dimer, leading to an opti-

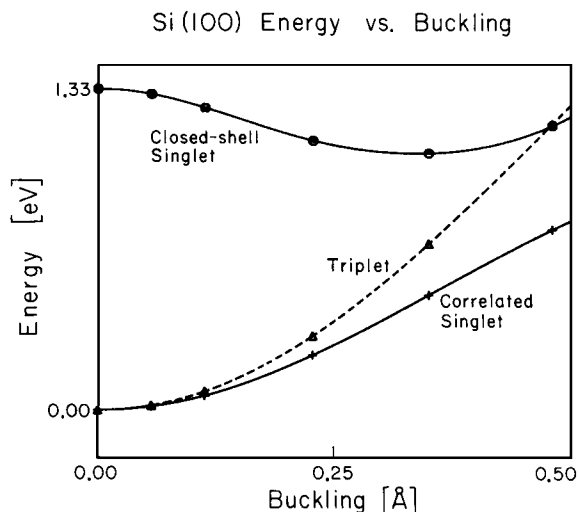


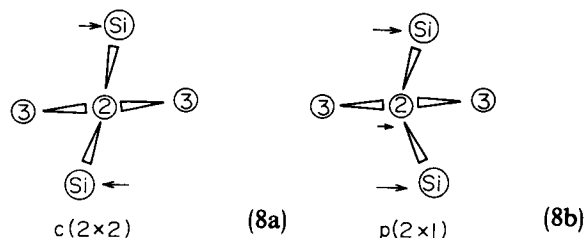
FIG. 4. Energy vs buckling curves for the HF singlet, HF triplet, and GVB singlet states of the dimer.

imum buckling of 0.33 Å. In semiempirical calculations, Chadi<sup>4</sup> has obtained bucklings varying from 0.45 to 0.65 Å. Verwoerd<sup>5</sup> has also found a buckling of 0.24 Å, and Yin and Cohen<sup>18</sup> found a buckling of 0.07 Å. *This buckling obtained for the HF-like singlet state is merely an artifact of the lack of electron correlation; introduction of electronic correlation, as in the GVB description, completely removes the buckling.*

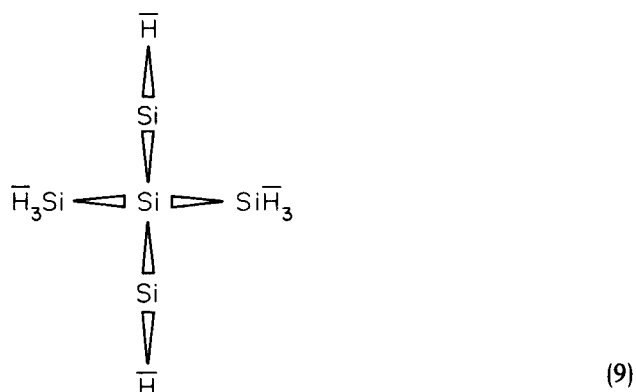
### C. Subsurface couplings

In the above calculations, the subsurface atoms were fixed. As indicated in Fig. 1, surface atoms represented by surface siligens were moved so as to correspond to a  $c(2 \times 2)$  distortion. In this cluster model, a  $(2 \times 1)$  distortion cannot be done because the siligen atoms, indicated as H, in Fig. 1, should be bonded for this structure, but this would not be possible for the cluster model. For the reconstructed surface

the major difference between  $c(2 \times 2)$  and  $(2 \times 1)$  is that in  $c(2 \times 2)$  the surface distorts to a pure twist about the subsurface atom (8a):



whereas in the  $(2 \times 1)$  distortion (8b) there is a bend toward the third-layer atoms. In (8b), the subsurface atom 2 is expected to move to the right. To obtain estimates of the energies for these distortions, we used the model



and moved the surface atoms by the distortion corresponding to the optimum singlet structure. We find that the  $2 \times 1$  distortion (8b) is 0.035 eV/subsurface atom lower in energy than the  $c(2 \times 2)$  structure (8a). Thus, the  $p(2 \times 1)$  distortion is favored by 0.07 eV/dimer. In the  $p(2 \times 1)$  distortion, we find that the second layer Si moves laterally by 0.056 Å, as indi-

Effect of buckling on dangling bond orbitals

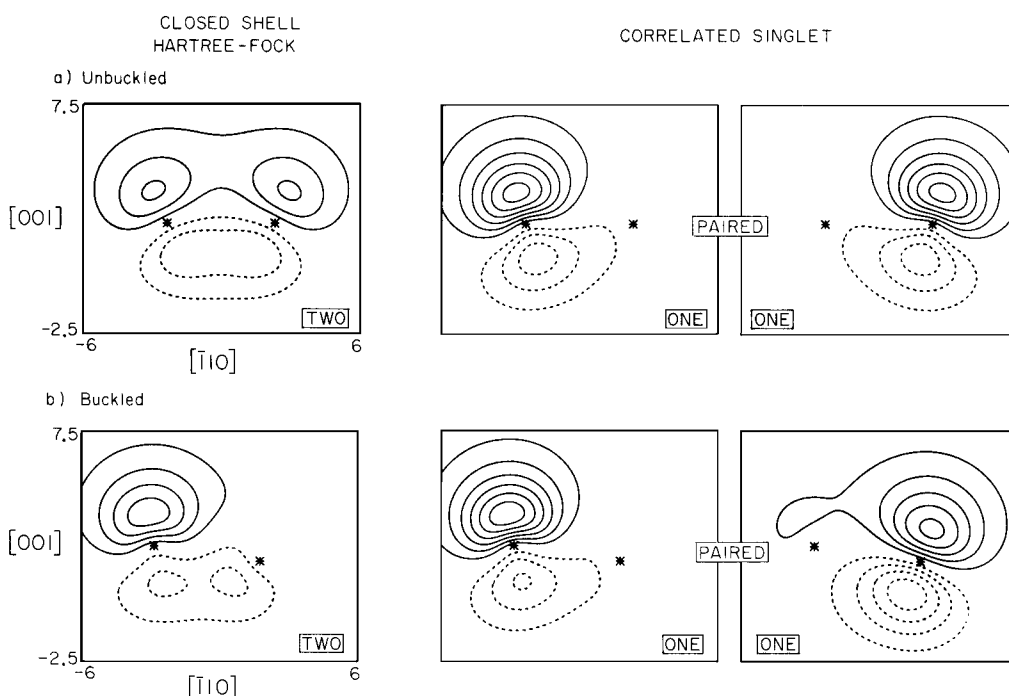


FIG. 5. Comparison of the dangling bond orbitals for the HF and GVB descriptions for the symmetric dimer and the buckled dimer. The amplitude plots are as in Fig. 3. The buckled orbitals are plotted for a buckling of 0.35 Å.

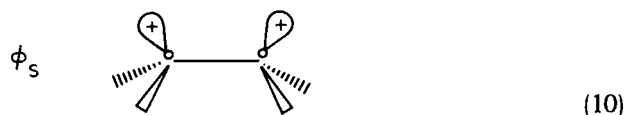
cated in (8b).

These results that the  $p(2 \times 1)$  structure is more stable than the  $c(2 \times 2)$  structure are consistent with all available experimental data. Unfortunately, the cluster models used here do not allow us to assess more complicated distortions, such as  $p(2 \times 2)$  and  $c(4 \times 2)$ . However, some speculations may be in order. Our calculations suggest that the singlet and triplet states are comparable in energy but involve very different geometries. A lower subsurface strain energy might be obtained for a structure having an alternation of singlet dimers and triplet dimers along a row of dimers [the 1 direction in  $p(2 \times 1)$ ]. This would lead to  $p(2 \times 2)$  and  $c(2 \times 4)$  structures, depending upon how the different rows are keyed with respect to each other. In this case, there might be good order along a dimer row but considerable disorder in the keying of different dimer rows, leading to the diffuse pattern observed in He atom scattering.<sup>10,17</sup>

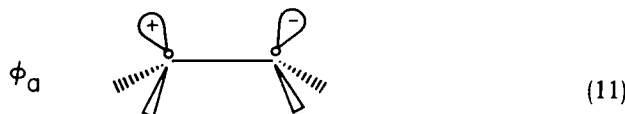
#### IV. DANGLING BOND SURFACE BANDS

The GVB calculations lead to a ground singlet state for each dimer. Considering an infinite surface, this leads to a nondegenerate singlet ground state for the whole system. In contrast, the closed-shell HF description for the symmetric dimer would lead to a half-filled band and hence to a metallic ground state for the surface.<sup>1-4</sup> The photoemission studies of Himpsel and Eastman<sup>8</sup> show a semiconducting surface and hence provide strong evidence against the description obtained by closed-shell HF.

In the GVB description of the dimer, the low-lying positive ion states have the form



(10)



(11)

corresponding to just the sum and difference of dangling bond orbitals.

Using the ground state geometry, we calculate that these levels are split by 0.50 eV, with the  $\phi_s$  state lower (smallest ionization energy). (In all calculations discussed in this section, we have solved for the final positive ion states self-consistently, including all valence electrons of the cluster and including electron correlation in the surface orbitals.) This is in excellent agreement with the angle-integrated photoemission,<sup>8</sup> which indicates that the two lowest surface bands whose peaks are split by 0.5 eV.

We also find that the ionization out of the dimer Si-Si bond is low lying. This leads to a final state with a singly occupied (symmetric) Si-Si orbital  $\bar{\phi}_s$ , along with two singly occupied dangling bond orbitals  $\phi_l$  and  $\phi_r$ . The result is three states<sup>15</sup>

$${}^4\Psi_A = \mathcal{A} \{ [\phi_l(1)\phi_r(2) - \phi_r(1)\phi_l(2)] \bar{\phi}_s(3) \alpha(1)\alpha(2)\alpha(3) \}, \quad (12)$$

$${}^2\Psi_S = \mathcal{A} \{ [\phi_l(1)\phi_r(2) + \phi_r(1)\phi_l(2)] \bar{\phi}_s(3) \alpha(1)\beta(2)\alpha(3) \}, \quad (13)$$

$${}^2\Psi_A = \mathcal{A} \{ [\phi_l(1)\phi_r(2) - \phi_r(1)\phi_l(2)] \bar{\phi}_s(3) \{ 2\alpha(1)\alpha(2)\beta(3) - [\alpha(1)\beta(2) + \beta(1)\alpha(2)]\alpha(3) \} \}, \quad (14)$$

where  $\mathcal{A}$  is the antisymmetrizer. The state (12) has all three singly occupied orbitals coupled to high spin  $S = 3/2$ . State (13) has the dangling bond orbitals singlet-paired, whereas state (14) has these orbitals triplet-paired; in both cases the total spin is  $S = 1/2$ . The subscript S or A indicates that the state is symmetric or antisymmetric with respect to the midpoint of the dimer bond. Starting with the singlet state of the dimer, the transitions to the  ${}^4\Psi_A$  and  ${}^2\Psi_A$  states are forbidden. We find the  ${}^4\Psi_A$ ,  ${}^2\Psi_S$ , and  ${}^2\Psi_A$  states at 1.3, 1.7, and 2.2 eV with respect to the  $\phi_s$  (10) ion state, whereas, experimentally,<sup>8</sup> there is a third surface band at 1.3 eV, in fair agreement with our results.

The above analysis involved only one dimer. To obtain the dispersion in the surface bands, we must calculate the coupling between ionizations on nearby dimers. We have not carried out such calculations but expect that we would obtain weak couplings (perhaps  $\sim 0.2$  eV) and hence a small dispersion on the surface. Himpsel and Eastman<sup>8</sup> suggest a dispersion of 0.5 eV; however, these spectra can be interpreted in terms of two slightly dispersed bands ( $< 0.2$  eV) if the shoulder observed for  $\Gamma$  is considered as the second band  $\Phi_a$  (it is observed 0.5 eV below the first band  $\phi_s$  as calculated). A test of this assignment would be to vary the incidence of the photon beam. Thus, for  $\Gamma$ , a photon beam at grazing inci-

dence should lead only to the upper band ( $\phi_s$ ), whereas a photon beam perpendicular to the sample should lead only to the second band ( $\phi_a$ ).

The observed spectrum shows that the third band at 1.3 eV (with respect to  $\phi_s$ ) has also very little dispersion, as might be expected for the dimer Si-Si ionizations.

Our calculations on clusters yield directly absolute ionization potentials (IP) for the surface dangling bond orbitals. Thus, we find the lowest IP state at 5.99 eV (however, we do not calculate the full energy bands). On the other hand, the experimental values are easily related to the Fermi energy,<sup>8</sup> with the lowest IP state at 0.7 eV below the Fermi energy. Taking the work function to be<sup>19</sup> 4.9 eV, we obtain an absolute IP of 5.6 eV, so that the calculated IP is about 0.4 eV too high.

#### V. Si(2p) CORE LEVELS

We have carried out calculations to determine the Si(2p) core levels for the surface atoms. Since these silicons have a different geometry and different effective charge than the bulk atoms, we would expect to observe a chemical shift of the Si(2p) core levels (relative to the bulk). In the present case, there are two equivalent silicons per (symmetric) dimer and

TABLE II. Silicon ( $2p$ ) core level ionization potentials (in eV) for the surface Si of the  $\text{Si}_9\bar{\text{H}}_{12}$  cluster model of the Si(100) surface. All energies are referenced to the calculated<sup>a)</sup> value for bulk Si. Positive values mean higher ionization potentials.

(a) No spin-orbit coupling			
State	Singlet geometry	Triplet geometry	
$^2\bar{\sigma}$	+ 1.73	+ 1.27	
$^2\bar{\pi}_{a'}$	+ 0.66	+ 0.48	
$^2\bar{\pi}_{a''}$	+ 0.54	+ 0.47	
$^4\pi_{a'}$	+ 0.50	+ 0.28	
$^2\pi_{a'}$	+ 0.45	+ 0.36	
$^2\pi_{a''}$	+ 0.36	+ 0.33	
$^4\pi_{a''}$	+ 0.31	+ 0.19	
$^2\sigma$	+ 0.03	+ 0.09	
$^4\sigma$	- 0.05	- 0.02	
(b) With spin-orbit coupling <sup>b)</sup>			
State	Experimental observation <sup>c)</sup>	Singlet geometry	Triplet geometry
$^2\bar{\sigma}_{1/2}$	No	+ 1.78	+ 1.34
$^4\pi_{3/2}$	⊥	+ 1.00	+ 0.82
$^2\bar{\pi}_{1/2}$	No	+ 0.81	+ 0.68
$^2\pi_{1/2}$	⊥	+ 0.67	+ 0.63
$^4\pi_{1/2}$	⊥	+ 0.62	+ 0.46
$^2\bar{\pi}_{1/2}^+$	No	+ 0.46	+ 0.35
$^4\pi_{1/2}^+$	⊥	+ 0.23	+ 0.09
$^2\pi_{1/2}^+$	⊥	+ 0.20	+ 0.14
$^2\pi_{1/2}^-$	⊥	- 0.03	+ 0.01
$^4\sigma_{1/2}$		- 0.10	- 0.08
$^4\sigma_{3/2}$		- 0.11	- 0.16
$^4\pi_{3/2}^+$	⊥	- 0.21	- 0.38

<sup>a)</sup> Reference 11.

<sup>b)</sup> Spin-orbit constant  $\lambda = -0.41$  eV from Ref. 9.

<sup>c)</sup> No means a spin-forbidden transition, ⊥ means photon incidence perpendicular to the surface, and || means grazing photon incidence.

two different geometries to consider (singlet and triplet). To investigate these effects, we calculated core ionizations at one of the surface silicons in the  $\text{Si}_9\bar{\text{H}}_{12}$  cluster. In these calculations, we included the core electrons of the surface Si and solved self-consistently for all electrons of the cluster after ionizing the Si( $2p$ ) orbital. This was done for all three possible  $2p$  states of Si. We then carried out a CI calculation including the final  $2p$  hole and the surface dangling bond orbitals, leading to a quartet and two doublet states for each of the three possible  $2p$  core holes.

In order to understand the results, it is useful to consider the following. First, there is an anisotropic chemical environment at the surface atom with local  $C_s$  symmetry. This leads to three core holes, two with symmetry  $a'$  (symmetric) and one with symmetry  $a''$  (antisymmetric); these are denoted as  $(2p)\sigma$  (core hole perpendicular to the surface, along the [001] direction),  $(2p)\pi_{a'}$  (core hole parallel to the  $[\bar{1}10]$  direction),  $(2p)\pi_{a''}$  (core hole parallel to the [110] direction), respectively. Second, for each core hole, the two dangling bond orbitals on the surface can be paired with the core hole to form two doublets and a quartet. Thus (ignoring spin-orbit coupling), we end up (for a given geometry) with nine Si( $2p$ ) levels:  $^2\sigma$ ,  $^2\bar{\sigma}$ ,  $^4\sigma$ ,  $^2\pi_{a'}$ ,  $^2\bar{\pi}_{a'}$ ,  $^4\pi_{a'}$ ,  $^2\pi_{a''}$ ,  $^2\bar{\pi}_{a''}$ , and  $^4\pi_{a''}$  (see Table II).

When we include the spin-orbit interaction, these nine levels split up into 12 levels:  $^2\bar{\sigma}_{1/2}$  at 1.78,  $^4\pi_{3/2}$  at 1.00,  $^2\bar{\pi}_{1/2}$  at 0.81,  $^2\pi_{1/2}$  at 0.67,  $^4\pi_{1/2}$  at 0.62,  $^2\bar{\pi}_{1/2}^+$  at 0.46,  $^4\pi_{1/2}^+$  at 0.23,  $^2\pi_{1/2}^+$  at 0.20,  $^2\pi_{1/2}^-$  at -0.03,  $^4\sigma_{1/2}$  at -0.10,  $^4\sigma_{3/2}$  at -0.11, and  $^4\pi_{3/2}^+$  at -0.21 eV. These values are for the singlet geometry and are given with respect to the bulk calculated<sup>11</sup> IP of 105.39 eV. All these states are doubly degenerate. The spin-orbit constant was taken to be  $\lambda = -0.41$  eV from the experimental bulk splitting.<sup>9</sup>

The states labeled as  $^2\bar{\sigma}$  and  $^2\bar{\pi}$  in Table II involve a triplet pairing of the surface dangling bond orbitals. Since the ground state has singlet coupling, these transitions are not allowed. Thus, there should be four groups of transitions observed for the surface core levels. The relative positions (and intensities in parentheses) are

$$0.0(4); 0.3(2), 0.8(2), \text{ and } 1.1(1) \text{ eV.}$$

The experimental spectrum<sup>9</sup> shows one clear band of surface levels shifted by -0.5 eV with respect to the bulk (to lower IP), with additional evidence for surface states obtained from deconvolutions that assume a 0.6-eV spin-orbit coupling is maintained at the surface. As indicated in Table II, we find that the surface spin-orbit splittings are considerably modified from those of the bulk, and hence it is not clear how much one can rely on the deconvolution. However, Ref. 9 does provide clear evidence for some surface features near +0.4 eV [see Fig. 1(a) of Ref. 9] and near -0.3 eV [see Fig. 2(a) of Ref. 9]. Thus, the theoretical and experimental splittings are comparable.

A test of our results would be to vary the orientation of the photon beam. The lowest group should be favored by grazing incidence, whereas the other groups should be favored by perpendicular incidence.

## VI. CONCLUSIONS

We have shown that the use of doubly occupied orbital wave functions, such as the closed-shell HF, artificially lead to an asymmetric dimer description of the Si(100) surfaces. The inclusion of the proper electron correlation produces a symmetric dimer description of the surface. We also show that there are two low-lying states of the neutral surface dimers, a singlet and a triplet, which are almost degenerate in energy (for a symmetric dimer), with the singlet state slightly lower than the triplet state. From energy minimization calculations, we conclude that the  $(2 \times 1)$  structure is favored over the  $c(2 \times 2)$ . We also show that our calculations for IP's for surface and Si( $2p$ ) core electrons are consistent with the current experimental results. Predictions from our calculations suggest further experimental tests.

## ACKNOWLEDGMENT

We acknowledge support of this work by a contract (No. N00014-79-C-0797) from the Office of Naval Research.

<sup>a)</sup> Contribution No. 6596.

<sup>1</sup>J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. **35**, 729 (1975); Phys. Rev. B **15**, 2408 (1977); J. A. Appelbaum and D. R. Hamann, Surf. Sci. **74**, 21 (1978).

<sup>2</sup>G. P. Kerker, S. G. Louie, and M. L. Cohen, Phys. Rev. B **17**, 706 (1978); J.

- Ihm, M. L. Cohen, and D. J. Chadi, *ibid.* **21**, 4592 (1980).
- <sup>3</sup>J. Pollmann and S. T. Pantelides, *Phys. Rev. B* **18**, 5524 (1978).
- <sup>4</sup>D. J. Chadi, *Phys. Rev. Lett.* **43**, 43 (1979); *J. Vac. Sci. Technol.* **16**, 1290 (1979).
- <sup>5</sup>W. S. Verwoerd, *Surf. Sci.* **99**, 581 (1980).
- <sup>6</sup>R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959); F. Jona, H. D. Shih, A. Ignatiev, D. W. Jepsen, and P. M. Marcus, *J. Phys. C* **10**, L67 (1977).
- <sup>7</sup>T. D. Poppendick, T. C. Ngoe, and M. B. Webb, *Surf. Sci.* **75**, 287 (1978).
- <sup>8</sup>F. J. Himpsel and D. E. Eastman, *J. Vac. Sci. Technol.* **16**, 1297 (1979); D. E. Eastman, *ibid.* **17**, 492 (1980).
- <sup>9</sup>F. J. Himpsel, P. Heimann, T. -C. Chiang, and D. E. Eastman, *Phys. Rev. Lett.* **45**, 1112 (1980).
- <sup>10</sup>M. J. Cardillo and G. E. Becker, *Phys. Rev. Lett.* **40**, 1148 (1978); *Phys. Rev. B* **21**, 1497 (1980).
- <sup>11</sup>A. Redondo, W. A. Goddard III, C. A. Swarts, and T. C. McGill, *J. Vac. Sci. Technol.* **19**, 498 (1981); A. Redondo, W. A. Goddard III, and T. C. McGill, *Phys. Rev. B* **24**, 6135 (1981); *J. Vac. Sci. Technol.* (in press)
- <sup>12</sup>A. Redondo, W. A. Goddard III, and T. C. McGill, *Phys. Rev. B* **15**, 5038 (1977); A. K. Rappé, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.* **85**, 1662 (1981).
- <sup>13</sup>W. A. Goddard III and T. C. McGill, *J. Vac. Sci. Technol.* **16**, 1308 (1979), and references therein.
- <sup>14</sup>A. Redondo, Ph.D. thesis, California Institute of Technology, 1976 (unpublished).
- <sup>15</sup>Ignoring normalization.
- <sup>16</sup>This is consistent with the LEED results of Lurie and Wilson [P. G. Lurie and J. M. Wilson, *Surf. Sci.* **65**, 453 (1977)]. See, also, W. S. Verwoerd, *ibid.* **103**, 404 (1981).
- <sup>17</sup>Recently, W. S. Yang, F. Jona, and P. M. Marcus (to be published) have carried out LEED intensity analyses on new data for Si(100)-(2×1) and find best fits for a buckled model (buckling = 0.4 Å) with a dimer distance of 2.54 Å. In addition, Tromp and co-workers [R. M. Tromp, R. G. Smeenk, and F. W. Saris, *Solid State Commun.* **39**, 755 (1981)] have concluded, from a comparison of experimental results with computer simulations of ion scattering, that the surface is reconstructed in asymmetric dimers. We feel that our model, which may include mixtures of singlet and triplet states (with an average dimer distance of 2.57 Å), may also lead to good LEED fits and good agreement for the ion scattering results.
- <sup>18</sup>M. T. Uin and M. L. Cohen, *Phys. Rev. B* **24**, 2303 (1981). Although they use a pseudopotential plus the Wigner interpolation formula for exchange and correlation, their actual wavefunction includes only doubly occupied orbitals of the HF type. This also leads to a buckled dimer, albeit with a much smaller buckling.
- <sup>19</sup>J. E. Rowe and H. Ibach, *Phys. Rev. Lett.* **32**, 421 (1974); J. E. Rowe, *Phys. Lett. A* **46**, 400 (1974).