Electron correlation in the Si(100) surface

Óscar Paz,1 António J. R. da Silva,2 Juan José Sáenz,1,3 and Emilio Artacho1,3

1 Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma, 28049 Madrid, Spain
2 Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 - São Paulo, SP Brazil
3 Instituto Nicolás Cabrera, Universidad Autónoma, 28049 Madrid, Spain

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Motivated by the controversy between quantum chemists and solid-state physicists, and by recent experimental results, spin-polarized density-functional (DFT) calculations are used to probe electron correlation in the Si(100) reconstructed surface. The ground state displays antiferromagnetic spin polarization for low dimer inclinations indicating, not magnetic order, but the importance of Mott-like correlations among dangling bonds. The lowest energy corresponds to a higher dimer inclination with no spin. DFT energies, however, should be taken with caution here. Our results together with quantum-chemical findings suggest dimers with highly correlated electrons that tend to buckle due to interactions with other dimers.

The freshly cut (100) surface of silicon has two dangling bonds per Si atom. This is a highly unfavorable configuration, and the surface reconstructs forming rows of dimers, thereby reducing the number of dangling bonds by a half. This chemical description is clear and well established, but the physics of the remaining two dangling bonds per dimer is not. The main reason is that the $\sigma$-like chemical bonds in silicon are well described by many electronic-structure methods, whereas the dangling bonds are much more subtle. The early argument for asymmetric dimers based on relating symmetric dimers to metallic character was found to be incorrect, since it is possible to obtain a symmetric, non-metallic state within a Hubbard like framework. However, experimental evidence accumulated afterwards strongly suggesting the asymmetry of the dimers. In addition, solid-state first-principles calculations based on the local-density approximation (LDA) to density-functional theory (DFT) converged to results in agreement with experiments. The dimer asymmetry was rationalized in chemical terms, the driving force staying within each dimer: a rehybridization of the orbitals with a charge in chemical terms, the driving force staying within each dimer. The asymmetric dimers are asymmetric it is because of reasons extrinsic to the dimer, i.e., interactions among dimers. The dimers would display important Mott-like (antiferromagnetic) correlations, and there would be no driving force towards asymmetry within the dimer.

Spin polarization is the simplest way to assess the importance of Mott-like correlations. A spin-polarized wave-function tends to the right dissociation limit, except for the fact that the spin symmetry is artificially broken. A spin-polarized DFT study of the surface is presented below. The polarization itself is to be interpreted as an indication of the need of a better treatment of dynamical correlations, and, therefore, the numbers are to be taken with caution. The magnetic order is artificially imposed and of no relevance to the point, except as a way of describing the short range correlations.

The DFT calculations were made using the numerical atomic-orbital (NAO) method in the SIESTA code implementation. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof to Kohn-Sham theory was the functional for exchange and correlation, except for the LDA tests.
shown below. Core electrons were replaced by norm-conserving pseudopotentials\(^{19}\) in their fully non-local formulation\(^{20}\). Valence electrons were described using a double-$\zeta$ polarised basis set of numerical atomic orbitals with a range defined by an energy shift of 200 meV, and a variationally optimized splitnorm of 0.3\(^{15}\). A uniform real-space mesh with a plane-wave cutoff of 80 Ry was used for numerical integration.

Calculations were performed for the 2×1, p(2×2) and c(4×2) reconstructions of Si(100) using a repeated slab geometry with nine layers of silicon and a layer of hydrogen atoms saturating one of the sides of the slab. The H-Si bonds were relaxed in a bulk-like saturated slab with H on both surfaces, using the bulk lattice parameter obtained within the theoretical framework described above. Then, one of the surfaces was kept saturated and fixed, including the H layer and the closest Si layer. The remaining eight layers were allowed to relax freely in all the calculations described below. Relaxations were considered to be finished when the maximum residual force was below 0.02 eV/Å. The forces on the fixed layers always stayed ≤0.06 eV/Å. Integrations over the first Brillouin zone were approximated by Monkhorst-Pack\(^{21}\) sets of $k$-points for a length cutoff of 15 Å\(^2\), which corresponds to a 4×8×1 set in the 2×1 geometry.

To test the methodology we have reproduced earlier results obtained with LDA. For bulk silicon a lattice parameter of 5.40 Å is obtained, which compares very well with the experimental value of 5.43 Å\(^2\) and with 5.37-5.38 Å of LDA plane-wave (PW) calculations\(^{24,25}\). The bulk modulus is 95 GPa employing the Murnaghan equation of state\(^{27}\) and 96 GPa using a quartic fit, to be compared with 99 GPa of experiment\(^{23}\) and 96-98 GPa of PW\(^{21,22}\). Table I shows the relevant magnitudes obtained for the 2×1, p(2×2) and c(4×2) reconstructions as compared with the figures obtained from LDA calculations of other groups. Spin polarized results for LDA were never reported, probably because the calculations converged to non-polarized. We obtain non-polarized results within LDA.

The spin-polarized GGA results of the present study are summarized in Fig. 1 for the p(2×2) geometry, where the relevant magnitudes are plotted versus dimer buckling. The buckling angle was imposed as a constraint in each calculation, with the rest of the system’s degrees of freedom being free to relax. As can be observed from Fig. 1, the most stable configuration remains unpolarized, as in the LDA calculation, with asymmetric dimers of 18.5° of inclination. At small buckling angles (≤6.1°) the system has a polarized, antiferromagnetic (AF) ordered solution with a lower energy than the non-polarized solution (0.07 eV/dimer decrease at 0°). $E(\alpha)$ seems to show a shallow minimum around the symmetric configuration. The dimer bond length increases with the spin polarization. The shorter bond length of 2.32 Å of the unpolarized solution can be understood in terms of the (artificial) reinforcing of the bond (double-bond) in the dimer, essentially absent in the polarized solution, for which a typical Si bond length of 2.35 Å is obtained. The subsurface lateral relaxation correlates with the inclination, but also with the dimer bond length.

A magnetic moment of 0.47 µ$_B$ is obtained at 0° inclination for this AF configuration. For a 2×1 unit cell there are two additional spin-polarized solutions: a ferromagnetic (F) spin configuration, and a mixed one, AF within the dimer and F among dimers in a row. Their energies are higher than the AF and are shown in Fig. 1(a). The magnetic moments are 0.51 µ$_B$ and 0.35 µ$_B$ for the mixed and F configurations, respectively. Interestingly, the dimer bond lengths are 2.31 Å and 2.33 Å for the mixed and F configurations, respectively, shorter than in the AF case.

These results confirm the importance of Mott-like electronic correlations in this surface. The results do not tell, however, about the intrinsic or extrinsic origin of the buckling that appears. Interdimer interactions that can make a difference are: (i) electrostatic: each dimer has...
a polarizability that can enhance or depress the dipole of an electric dipole due to its charge transfer \[2,34,35\] and a polarizability that can enhance or depress the dipole when interacting with its neighbors; (ii) surface deposition: the relative disposition of dimers can relax surface stress as pointed out by García and Northrup \[12\]; (iii) electronic hopping: the electron delocalization among dangling bonds of different dimers can depress electronic correlations and change the energy.

The first point can be discarded by noting that it has opposite effect on the energy for the asymmetric \(2\times1\) and \(p(2\times2)\) surfaces. The difference between these two structures is in the relative disposition of neighboring dimer inclinations: in the \(2\times1\) all the dimers buckle in the same direction, in the \(p(2\times2)\) neighboring dimers in a row have opposite inclinations. The electric dipoles are mostly parallel and repelling in the \(2\times1\) order, and antiparallel and attracting in the \(p(2\times2)\). The effect should thus appear in the energy difference between the asymmetric \(2\times1\) and the \(p(2\times2)\) rather than in the difference between symmetric and asymmetric. This argument has been ratified by calculating the electrostatic interaction energy of a two-dimensional set of dipoles with the appropriate disposition and the dipolar moments extracted from the DFT calculations. The results confirm the order of magnitude and sign used in the argumentation: the \(2\times1\) disposition has positive energy, whereas the \(p(2\times2)\) has it negative, both having an order of magnitude of 0.1 eV/dimer for the maximum \(p(2\times2)\) charge transfer of 0.36 electrons.

It is tempting to use a similar argument for the effect of the surface stress: it seems reasonable to assume that by buckling the dimers the surface stress would behave in opposite manner for the \(2\times1\) configuration than for the \(p(2\times2)\) one. However, the calculations do not show that trend: the compressive stress in the direction of the dimer rows is highest for the symmetric-dimer surface, and lowest for the \(p(2\times2)\) structure. Surface stress could thus be playing a role in the destabilization of the symmetric dimers.

The effect of the electron delocalization among dimers cannot be assessed as easily. The subsistence of important correlation effects can be inferred from the fact that clusters with more than one dimer, when described within quantum-chemical methods that describe well the dynamical correlations, tend to stay symmetric \[12,36\]. However, to our knowledge, no high-level quantum-chemical calculation comparing the buckled against the non-buckled configurations, has been performed for clusters with more than two surface dimers. As has been shown recently by Penev et al. \[37\] this may be an important point, as discussed below. Penev et al. \[37\] help in discerning the issue of electron delocalization by comparing cluster calculations with slab calculations within the same level of theory otherwise. The asymmetry of the dimers is found to be very much favored in the extended system, the clusters with one or two surface dimers A showing a nearly flat behavior of energy versus buckling angle, \(E(\alpha)\), close to \(\alpha = 0°\). Part of the difference, however, could be due to the treatment of the relaxation.

![Figure 1](image-url)

**FIG. 1.** GGA results versus dimer inclination, \(\alpha\), with and without spin polarization. The curves are interpolations.

(a) Total energy (per dimer) with respect to the most stable \(p(2\times2)\) configuration. The full circles are for the ground state, which is spin polarized (AF) at small angles; empty circles show the unpolarized solution. The square is for the mixed AF-F configuration described in the text, and the diamond for the ferromagnetic configuration.

(b) Magnetic moment on each dimer atom in the AF configuration.

(c) Intradimer charge transfer \((Q_{\text{high}} - Q_{\text{low}})\), obtained from Mulliken population analysis.

(d) Dimer bond length.

(e) Displacement of subsurface atoms in the direction parallel to dimer rows.
Kang [38]. An approximation to the correlated constraints in the clusters, as pointed out by Yang and Kondo [54], the correlated motion of carriers in doped perovskites. On the Si(100) surface could be used to gain insights for many-body physics. There are thus cross-breeding Hamiltonians used for completely different problems in accessible techniques, and the model can be solved in different approximations to a high degree of accuracy. Results for it will be presented elsewhere [39]. It is interesting to note that such a Hamiltonian is remarkably close to Hamiltonians used for completely different problems in many-body physics. There are thus cross-breeding possibilities, and it would be quite interesting if knowledge on the Si(100) surface could be used to gain insights for the correlated motion of carriers in doped perovskites.

\[ E(\alpha) \approx E_{\text{corr}}^{\text{clus}}(\alpha) + [E_{\text{DFT}}^{\text{slab}}(\alpha) - E_{\text{DFT}}^{\text{clus}}(\alpha)], \]

where \( E_{\text{corr}}^{\text{clus}}(\alpha) \) is for the correlated cluster calculations, and \( E_{\text{DFT}}^{\text{slab}}(\alpha) \) and \( E_{\text{DFT}}^{\text{clus}}(\alpha) \) are for the slab and cluster DFT calculations, respectively. From the calculations of Penév et al. [37] one can estimate that the term \( [E_{\text{DFT}}^{\text{slab}}(\alpha) - E_{\text{DFT}}^{\text{clus}}(\alpha)] \) would give a maximum gain of the order of 0.2 eV/dimer towards buckling due to extrinsic dimer effects (comparing the slab with the Si\(_6\)H\(_{12}\) cluster calculation). To determine if the ground state has a buckled or non-buckled configuration one has to know \( E_{\text{corr}}^{\text{clus}}(\alpha) \) as a function of \( \alpha \) for a high-level correlated calculation. A more rigorous computation for the correlated extended system requires computation techniques not available at present. Given all that was discussed above, a DFT calculation, spin-polarized or not, should not be fully trusted in this respect.

Another possibility, which can also help to gain further insight about the correlation effects in this problem, would be the use of a model Hamiltonian for a single row of dimers, as the stripe or ladders that are being treated now for high \( T_c \) superconductors, as pointed out by Kondo et al. [54]. It would consist of a Hubbard-like model on the ladder, coupled to a classical dynamical variable describing the buckling. Parameters for this model can be obtained from suitable calculations with accessible techniques, and the model can be solved in different approximations to a high degree of accuracy. Results for it will be presented elsewhere [39].

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