Ab-Initio Calculations of Materials Properties

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Introduction

Predicting and understanding the properties and behavior of real materials systems is of great importance both from technological and academic points of view. The theoretical problems associated with these systems are, of course, quite complex. However, we are currently at the forefront of beginning to overcome many of these problems.

Our research is devoted to creating a realistic microscopic quantum mechanical description of the properties of real material systems. In the past, theoretical attempts to deduce microscopic electronic and geometric structure have been generally based on optimizing a geometry to fit known experimental data. Our approach is more fundamental: predicting geometric, electronic, and dynamical structure, *ab-initio* — that is, given *only* the atomic numbers of the constituent atoms as experimental input. Briefly, our method makes it possible to accurately and efficiently calculate the total energy of a solid by the use of density functional theory, pseudopotential theory and a conjugate gradients iterative minimization technique for relaxing the electronic and nuclear coordinates. *Ab-initio* investigations are invaluable because they make possible theoretical calculations or simulations that can stand on their own. They may complement experimental observations but need not be guided by experimental *interpretations*. Our objective is to obtain a fundamental, microscopic understanding of various physical and chemical phenomena of real materials systems.

1. Forming Logic Gates with Silicon Dimers

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Device miniaturization has been at the focus of modern semiconductor-based computer technology for decades. However, the limit to this downscaling is approaching very fast. If "Moore's law"[1] continues to hold, then by at least 2017, device features will have shrunk past a critical length where the device will no longer work under its current design. This is due to the difficulties in applying a fundamentally macro-scale architecture to nano-scale geometries. In anticipation of this limit, there has been active pursuit of alternative computing paradigms, which employ intrinsically nano-scale components. Some recent efforts include quantum-dot "cellular automata"[2], DNA computing [3,4], and molecular electronics [5]. While these mechanisms have shown some success in both theory and experiment, the difficulties of manipulating such small structures pose a significant barrier to both manufacturing and operation of actual circuits.

These difficulties can be avoided if there exist systems that, in some sense, *self-assemble* into logic gates. It might then be possible to use existing technology to exploit such a system into the basis of a computing paradigm. Through ab-initio modeling, we have identified such a system, and in this paper we describe it.

Si(100) forms rows of mechanically bistable dimers along the (011) direction as schematically shown in Fig. 1. [6,7,8] The barrier to flipping due to surface strain forces and local electronic configuration is high enough (~150 meV) to maintain bistability even at relatively high temperature (~100 K). Nevertheless, adjacent dimers are not altogether independent. The interaction between nearby dimers is effectively anti-ferromagnetic, resulting in a 4x2 ground state configuration.

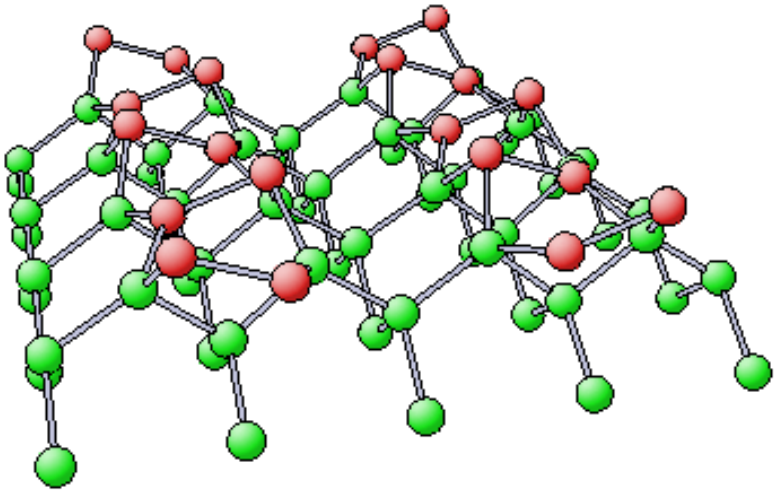

Figure 1. A ball and stick model of the relaxed Si(100) surface. The atoms making up the rows of buckled dimers are highlighted in red.

A few years ago, Cho and Joannopoulos [9] proposed a method of using the reconstructed Si(100) surface dimers as memory "bits," utilizing a tungsten scanning probe to perform read and write functions. The main advantage of this method is that the density of information approaches 420 Gbit/mm^2. The local flipping barrier resists the dimer-dimer interaction, thereby assuring information integrity, i.e., when the probe is removed, the dimer does not flip due to dimer-dimer interactions.

Our proposed method relies on the observation that the mechanism to resist interaction between nearby dimers can be selectively "turned off" by controlling the position of a scanning probe. Also, dimers can be individually deactivated by site-specific hydrogen passivation, e.g. using feedback-controlled lithography [10-12]. In this way, dimers can be forced to interact, and a computation can take place. After all, computation is, at its very basis, merely an *interaction* of information.

In the proposed scheme, the probe, e.g. an STM tip, serves as a catalyst for dimer flipping rather than an active agent, as in the dimer memory application. The position of the tip will be shown to be able to eliminate the energetic barrier for flipping, causing the local dimer-dimer interactions to be the dominant force in deciding the state of a "bit". Proper spatial patterning of H-passivated (unbuckled) dimers on the surface can define a specific hardware "program". A sufficiently complex program can define a universal computer, much in the same way the arrangement of transistors on a chip defines our modern electronic computers.

We fully realize the experimental difficulties inherent in this approach. Among these are the necessities for low temperatures and ultra-high vacuum. However, it is important to explore and identify potential new computing paradigms theoretically, in the hopes that the future state-of-the-art will eventually be capable of realizing such systems experimentally.

To establish the possibility of tip-induced dimer flipping, we have performed density functional total energy calculations in a conjugate-gradient scheme and the LDA approximation. We use separable atomic pseudopotentials to describe the electron-ion interaction and supercells to model the aperiodic surface [13-15]. We used an 11 Hartree planewave basis cutoff energy with at least 2x2x1 k-point sampling in the 4x3 surface unit cell. All calculations used a four-layer slab of silicon passivated with H atoms on one surface and a relaxed dimer reconstruction on the other surface. Due to periodic boundary conditions in all directions, approximately 10Å of vacuum was used separate adjacent slabs.

To study the in-row dimer-dimer interactions, we have passivated the dimers in neighboring rows with H. We have modeled the tungsten tip as a structure consisting of four W-atoms in a tetrahedra configuration. While the three base W atoms are held fixed, the tip W atom is allowed to move freely as in Ref. [9].

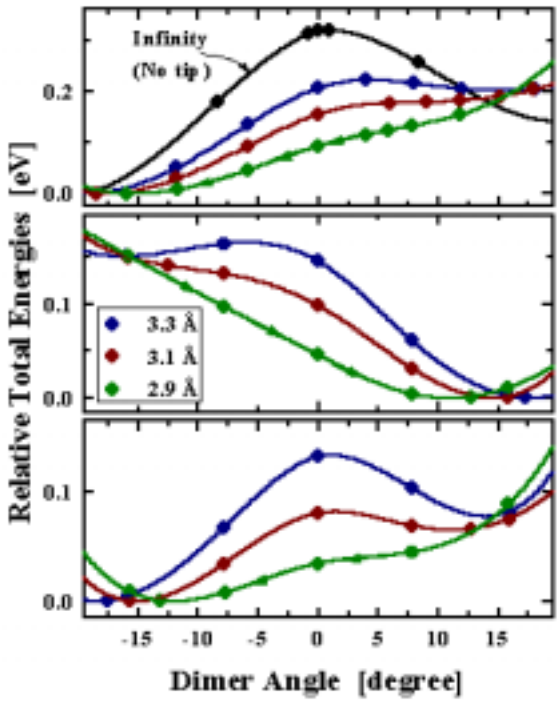

Figure 2. Total energy dependence on dimer angle at different tungsten scanning probe heights above the dimer. The calculated data are fit with a cubic spline to aid the eye. Because the exact position of the surface cannot be specified exactly, the heights labeling each curve are only approximate. However, the differences between the heights are exact. (Top): The scanning probe is lowered onto the midpoint of the dimer and the two neighboring dimers within the row are aligned. (Middle): The scanning probe is lowered onto a point ~0.2 Å from the dimer midpoint when the neighboring dimers are antialigned. Interpreting the neighboring dimer states as inputs to a logic gate, this corresponds to a (1,0) configuration as described in the text. (Bottom): With aligned neighboring dimers,

Figure 2 (top) shows total energy as a function of dimer angle as the tungsten tip is lowered onto

the midpoint of the dimer. The nearest neighbors within the dimer row are buckled in the same direction. In the absence of a probe, there exist two unequal minima separated by a barrier. The salient feature is that the bistability of the dimer can be eliminated by lowering the tip past a critical height, where there exists a unique energy minimum. Moreover, the details of the barrier elimination clearly allow a thermodynamically stable dimer state transition as the tip is lowered and then raised. Imagine the dimer in a state near +20 deg initially with the tip far away. As the tip is lowered, the initial energetic minimum disappears, and the dimer relaxes to a state near -20 deg. When the tip is raised, the initial minimum forms again, this time ~200meV higher than the new relaxed state. Even at high temperatures, this state is statistically inaccessible. Likewise, if the system starts out in the state near -20 deg., it stays there as the tip performs its cycle.

In order to perform arbitrarily complicated logic functions, we need a "complete" set of logic operations. One such set contains NOR, NOT, and COPY. [16] Using the basic idea illustrated above we can demonstrate the operation of a NOR gate, whose “truth table” is shown in Fig. 3 (top).

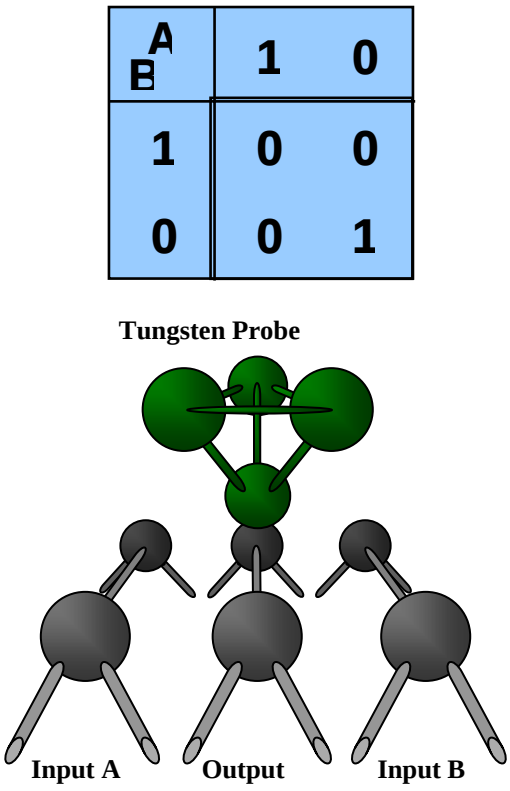

Figure 3. (Top): The “truth table” for a NOR gate. (Bottom): The NOR gate geometry and interpretation of each outside dimer as an input to a logic gate and the inside dimer as the output.

Consider the dimers adjacent to the dimer under the tip as inputs into the gate, while the dimer probed by the tip is the output, as schematically shown in Fig. 3 (bottom). In the case of identical inputs A and B, we can see from the above discussion that the output (after tip lowering and raising) will be NOT(A). When the two input bits are in opposite directions, however, the middle dimer will be in a frustrated configuration--its two minima will be equivalent. By lowering the tip in

an asymmetrical way, so that the middle dimer will be forced into one direction when the influences from the input dimers cancel each other, we can "pin" the dimer to a state determined by the position of the tip. However, we must take care that the asymmetry will not be so strong as to overpower the dimer-dimer interaction when the inputs are identical and the tip-dimer interaction opposes it.

By analyzing the tip height=Infinity total energy curve shown in Fig. 2 (top), we see an energy difference between the two minima of 150meV over a dimer angle of 40 degrees. Therefore, a reasonable estimate for the torque on the dimer due to interaction with other dimers is 200meV/rad. The partial W-Si bond, formed when the tip comes into intimate contact with the surface, gives rise to an attractive force acting on the surface of roughly 2eV/ Å. [9] This can be determined from the total energy change of the system as the tip height is changed at the typical distances in Fig. 2. Therefore the net torque on a dimer of radius ~1 Å is equalized if the tip lowering axis is moved to a distance on the order of 0.1 Å from the center of the dimer towards one of the ions. Our calculations have shown that placing the tip ~ 0.25 Å from the center results in a symmetric barrier lowering, which corresponds to effective canceling of the dimer-dimer and tip-dimer interactions. In practice, this would require an STM with tip positioning as precise as 0.1 Å. This precision is possible with most modern piezo position control.

We therefore moved the tip back slightly to ~ 0.2 Å from the center of the dimer. There are two requisite demonstrations before confirmation of NOR gate operation: first, that the dimer is successfully pinned when the inputs are opposite ((1,0) configuration and its symmetrically identical (0,1) configuration); and second, that the dimer will still flip as demonstrated above when the inputs agree and the interaction opposes the pinning force ((0,0) configuration). In the opposite case ((1,1) configuration), the pinning force only enhances the dimer-dimer interaction, in which case a demonstration is unnecessary.

Figure 2 (middle) shows total energy curves for the (1,0) configuration. In the absence of any net dimer-dimer interaction, the tip-dimer interaction sufficiently pins the dimer to a state which is ~150meV lower than the higher state, upon a cycle of tip lowering and removal. As in Ref. [9], the tip effectively "pulls" on the tilting dimer when the tip is removed. Hence, the output is determined by the side to which the tip is skewed, since the net dimer-dimer interaction is zero.

Figure 2 (bottom) shows a recalculation of the curves in Fig. 2 (top) with the tip shifted by 0.2 Å from the center of the dimer. The input dimers are aligned in the (0,0) configuration. Clearly, the tip-dimer interaction has had the effect of bringing the two minima closer to each other (c.f. Fig. 2(top)) by canceling out some of the dimer-dimer interaction. However, at a tip height around 3 Å the higher energy minimum disappears approximately 50meV above the other minimum. This allows thermodynamically stable dimer flipping at experimentally attainable temperatures.

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16. In traditional logic paradigms such as digital electronics, NOR forms a complete set of logic operations by itself. However, in that case the information propagates easily along conductive wires. Information encoded in a dimer state does not propagate from the output of one logic gate to another without external influence.

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