FIRST-PRINCIPLES ELECTRONIC STRUCTURE CALCULATIONS
WITH MOLECULAR DYNAMICS
MADE EASY

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The technique of quantum molecular dynamics is reviewed, and a simplified approach based on a first-principles tight-binding implementation of local density theory is discussed. Several illustrations and applications of the theory are presented. Applying it to amorphous materials, we have developed a procedure for producing amorphous Si networks with small defect concentrations. Benchmark checks are made for atomic geometries at Si(111)-(2x1) and Si(001)-(2x1), p(2x2), and c(4x2) reconstructed surfaces. A simulation of a Scanning Tunneling Microscope tip interacting with a reconstructed surface is performed, and it is shown how the tip can alter the reconstruction of the surface. Simulation of a kinked Si(001) surface step and comparison to an unkinked step are also presented.

I. Introduction

The decade of the '80's has seen an explosion of growth in the development and application of first-principles electronic structure methods and total energy calculations. These calculations give as output the energy levels, band structure, and total energy of the system from the input of the atomic number and the atomic positions. A wide variety of theoretical methods are used to perform such calculations, but most are based on the local density approximation (LDA).

One frontier of the '90's, which is just beginning to be crossed, is the ability to include the dynamics of the atoms in the electronic structure calculation. It is hoped that this will allow us to remove as input the positions of the atoms; rather the atomic positions are output. The atomic positions are in many cases what one really wants to know. For instance, one wants the position of the atoms at a reconstructed surface or of adatoms at a surface, the atomic coordinates and defect structures of amorphous materials, or even the atomic configuration of atoms in a molecule.

In this paper we discuss the method of quantum molecular dynamics, which allows the dynamics of the system to be probed simultaneously with the electronic structure of the system. The essence of the method can be expressed in an oversimplified way by describing it as a combination of the Schrödinger equation for the electrons,

$$H \ \Psi = \varepsilon \ \Psi,$$

with Newton's law of motion for the nuclei,

$$\vec{F} = m \ \vec{a}.$$

Applications of this melding together of classical and quantum physics are immense.

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Standard quantities can be investigated such as the band structure, phonon dispersion, charge density, and total energy. The introduction of forces and Newton's laws extends the range of possible quantities which can be investigated to anharmonic effects in phonon systems, ground and configurational excited state geometries, liquids, amorphous systems, non-equilibrium systems and so on. In all of this, a fundamental assumption is that the Born-Oppenheimer (adiabatic) approximation holds. This approximation assumes that the light electrons respond instantaneously to the motion of the heavy nuclei and are in the instantaneous ground state.

This paper will review the method of quantum molecular dynamics in section II. In Sections III-VII we present some applications of our method of quantum molecular dynamics which include studies of vibrational modes, amorphous Si structures, Si surface reconstructions, a Scanning Tunneling Microscope (STM) tip-surface simulation, and relaxation and energetics around a kinked Si(001) surface step.

II. Methods of Quantum Molecular Dynamics in Covalent Systems

The use of molecular dynamics using **empirical potentials** is not at all new. In 1959, Alder and Wainwright [1] published "Studies in molecular dynamics ..." using a square well potential. A whole school of work has been established following the work of A. Rahman [2]. Atomic (or 3-body or higher-body) potentials are still very much used today for simulations of very large systems containing hundreds to hundreds of thousands of atoms. In such a simulation an interaction between atoms is assumed, and the parameters of the interaction are generally fit to some experimental quantities. It was realized early that a simple two-body potential will not work well for a covalent system (such as Si or GaAs) since the interaction between atoms is quite unlike a central potential because of the directional nature of the electron-sharing among the atoms. To remedy this situation, higher-body interactions have been included [3-7] to mimic the natural tetrahedral bonding these systems prefer. Our experience with these potentials at surfaces however, has been quite disappointing. We have examined 2x1 reconstructions on Si(111) surfaces and find that none of the potentials we have tested give satisfactory results. Some claim to give a reconstructed surface as the minimum energy, but when used in a molecular dynamics simulation, we find a relaxed (1x1) surface is actually lower in energy. It may be too much to expect for a potential to predict geometries far from geometries in which they were fit, since electronic structure effects, which generally drive such reconstructions, are absent from the theory.

Quantum molecular dynamics simulations are orders of magnitude more difficult to perform than molecular dynamics simulations based on potentials. However, they properly incorporate the electronic states, so are more realistic, and contain a far more complete description of the system.

The first such calculation to include the electronic structure of a covalent system in a molecular dynamics simulation to our knowledge was submitted in 1985 by Sankey and Allen [8]. In this work, the electronic structure was considerably simplified by using an empirical tight-binding Hamiltonian of the Harrison et al. form [9]. The forces were determined by differentiating the electronic structure total energy by making use of the Hellmann-Feynman theorem. This approach was used to investigate (110) surface relaxation in 12 different semiconductors. Menon et al. [10] have developed a complementary approach using Green's functions. An empirical tight-binding approach has recently been used to study the anharmonic effects in high temperature Si and disorder and defects in Si [11], and for an Si_3 cluster and a Si(001) surface [12].

The empirical tight-binding method has the advantage of being very fast and easy to use. It typically uses only an sp^3 basis of orbitals for each of the two atoms, and so requires the diagonalization of a relatively small Hamiltonian matrix. Its chief disadvantage is that the matrix elements are adjustable parameters, adjusted to fit some experimental or theoretical observation. Its fundamental flaw however is that it is not based on any rigorous total energy theory, so that a total energy functional has to be guessed at or invented. Ion-ion interactions, and electron-electron interactions are included only approximately and phenomenologically by introducing some empirical short ranged potential.

The electronic structure methods developed during the '80's led Car and Parrinello [13] and others [14] to formulate their so called "unified approach" which follows the traditional approach of expanding the wavefunction in plane-waves in a periodic system. They use a fictitious Lagrangian for the electrons along with the true Lagrangian for the nuclei to follow the dynamics of the electrons and nuclei simultaneously. This technique avoids the diagonalization of super-large matrices which occur in plane-wave expansions. This technique has made no fundamental approximations, so that the level of accuracy previously enjoyed in static calculations ought to be present here as well. The disadvantage however is that the calculations are quite extensive, requiring huge computer resources. This limits the size and scope of the calculations that can be performed. Furthermore, these technical difficulties force hidden approximations to be made, such as the use of only the Γ point in Brillouin zone summations.

In this paper, we present recent results of quantum molecular dynamics simulations, which combine the simplicity of empirical tight-binding techniques, with the rigorous foundations of the LDA and the use of pseudopotentials. We have achieved this by developing an ab-initio tight-binding method optimized specifically for molecular dynamics. The electronic states of the system are written as a linear combination of pseudo-atomic-orbitals (PAO's) at each site. For the systems

we have studied so far (Si, Ge, and C), we include sp^3 orbitals on each site. The orbitals are obtained from a self-consistent LDA pseudopotential calculation of the free atom, but with the boundary condition that the wavefunction vanish at r_c, instead of the usual boundary condition that the wavefunction vanish at infinity. This slightly excites the atom from its ground state, and crudely represents confinement effects of the electron in the condensed system. Its real practical purpose however, is to introduce a cutoff for the range of wavefunction overlap and matrix elements between an atom and its neighbors. We have chosen r_c to be 5.0, 5.0, and 3.3 a_B for Si, Ge, and C respectively, which yields Hamiltonian matrix elements up to third neighbors in the bulk phases of these materials.

The total energy and electronic states are computed with the use of four major approximations. The first approximation is the LDA and the use of norm-conserving pseudopotentials for the valence electrons. The second is the use of PAO's in which to evaluate the first-principles tight-binding matrix elements. The third approximation is to replace the Kohn-Sham LDA self-consistent energy functional by the considerably simplified but approximate Harris [15] energy functional. Here the input charge density is a sum of neutral atom charge densities, and the output charge density is included to first order in the energy functional. Finally, the fourth approximation involves the evaluation of the matrix elements of the various terms of the Harris LDA Hamiltonian. Most terms are computed exactly, but some three-center integrals are constructed (nearly exactly) by multipole expansions, and the non-linear exchange-correlation matrix elements are evaluated in a mean-field-like approximation. All matrix elements are computed in advance and stored in tabulated form. The method combines the rigorous foundation of the LDA with the computational simplicity of the tight-binding method. It is a numerically fast procedure compared to any other first principles approach.

The method is performed entirely in real space, so that systems such as molecular clusters can be handled as easily as a periodic solid. Static quantities have been computed [16] such as the equilibrium lattice constant, bulk modulus, optic mode frequency, cohesive energy, band structure, and phase diagram as a function of volume for bulk Si, and equilibrium structures of small Si clusters. Excellent agreement is found with experiment and other calculations. Only a brief outline of the theory has been given here, but complete details including further motivation and derivations are given in Refs. [16] and [17]. We now briefly describe some applications of the method.

III. Vibrational Modes

A simple application of the method and a further test of the accuracy of the method is the determination of phonon dispersion curves of bulk Si with wavevector along the (100) direction. We consider a supercell of Si
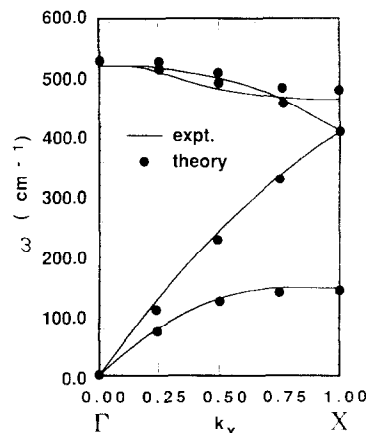

Figure 1. The phonon dispersion relations of Si obtained from the first-principles tight-binding method for k-vectors along (100), compared to experiment.

containing 16 atoms. The unit cell is a long thin rectangular parallelepiped with the long axis along (100) and short axes along (0 -1 1) and (0 1 1). The atoms are started from their equilibrium positions and given random velocities. They will vibrate as a mixture of transverse and longitudinal modes whose wavevectors "fit" into the Brillouin zone along the (100) direction, for a supercell which is four lattice periods long. The frequencies as a function of wavevector and polarization are obtained from the velocity-velocity autocorrelation function. The frequency dispersion relations at low temperature compared to experiment are shown in Figure 1. The agreement with experiment is excellent over the whole range. Notice that the flattening of the acoustic transverse modes near X is well reproduced. We emphasize that no fitting of parameters of any kind was done. Furthermore, the use of dynamical matrices or of the harmonic approximation is also not needed.

IV. Amorphous Si

The first-principles tight-binding molecular dynamics technique has been used to model defects, disorder, and structure in amorphous Si. We review here some of our major findings.

Theoretically, a:Si networks are constructed by quenching randomly disordered or partially melted Si to form a condensed, but disordered system in a local (metastable) minimum energy configuration. A general feature of all molecular dynamics simulations of amorphous Si to date is that the concentration of defects is too large. Experimentally a:Si can be made with a few percent defects, while simulations generally produce ~20% defects. In our simulations, we noted that a sample, initially with little disorder, always reverted back to a perfect crystal (0% defects) during quenching.
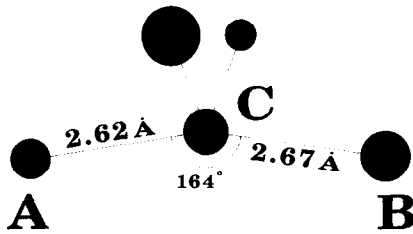
Figure 2. Geometry of the "pseudo-defect" containing badly strained, but four-fold coordinated, atoms. This pseudo-defect remains stable in the amorphous solid and has a deep level in the gap.

With complete disorder, the sample finds a local minimum after quenching with 15-25% defects. With this in mind, we have developed a procedure [18][19] which uses an intermediate region between little disorder and complete disorder, which when quenched to a local minimum, yields a small concentration of defects as found in experiments. Specifically, a 64 atom supercell of amorphous Si is found with a ~6% concentration of defects corresponding to two dangling bonds (three-fold coordinated atoms) and two floating bonds (five-fold coordinated atoms). Annealing this sample at room temperature for some time and then quenching, we find that this sample converts to a two defect sample of two dangling bonds, and hence a concentration of ~3% defects. This two defect sample however, had three levels in the gap. Two of them were from the two dangling bonds, and the third was from the "pseudo-defect" shown in Figure 2. This pseudo-defect would not normally be considered a defect since each of the atoms has four neighbors. The central atom (labeled C) has two near-normal neighbors with bulk-like Si bond-lengths (~2.35Å) and two neighbors (labeled A and B) which are stretched away from C with a large opening angle of 164°. The deep level wavefunction of this pseudo-defect is highly localized nearly uniformly on atoms A, B, and C. Such large strained bonds may play an important role in band tailing states of a:Si.

V. Surface Reconstructions

In order to simulate a reconstruction at a surface, we first create an atomic basis, or supercell, which is subject to periodic boundary conditions in the plane of the desired surface. The size of the basis depends on the size of the reconstruction to be studied (e.g., 2x1, 2x2, 4x2, etc.), and on the number of atomic layers in the slab deemed necessary (usually five or six). The slabs are isolated, and unlike plane-wave methods, there is no large-distance periodic repetition of the slabs normal to the surface.

At the surface (the top-most atomic layer), dangling bonds are left free to drive the reconstruction. On the bottom-most layer, however, we simulate connections to the bulk.

The atoms in this layer are made very massive, so that they are unable to move, and their dangling bonds are "tied off" with hydrogen atoms.

The molecular dynamical relaxation is usually done by dynamical quenching; i.e., whenever the kinetic energy passes a local maximum (thus the potential energy passes a local minimum) the kinetic energy is set to zero. This process is repeated until the system is stable and all forces are zero.

Si(111)-(2x1)

The starting point for the reconstruction process of the Si(111)-(2x1) surface is the terminated bulk Si(111) surface (six layers deep) in a 2x1 unit cell. In terminating the bulk, we have "cut" the bonds which lie in the (111) direction. We allowed the system to vibrate at room temperature for 100 time steps (about 0.25 ps) and then dynamically quenched. The final state given after quenching is in agreement with Pandey's π-bonded chain model [20] for the Si(111)-(2x1) surface (Figure 3).
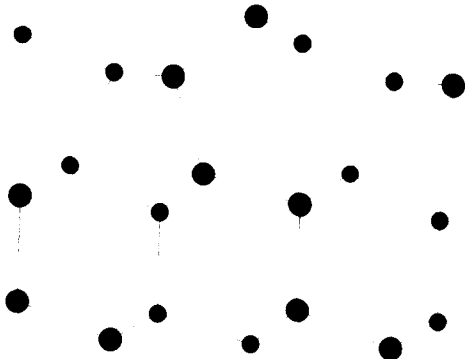

Figure 3. Final state of Si(111) surface reconstruction - Pandey π-bonded chain model.

An intermediate state in the reconstruction is Haneman's buckling model [21]. Passing from the metastable Haneman model to the Pandey model requires breaking a bond in a six-membered ring followed by a rebonding to form five- and seven-membered rings. It should be emphasized that this process occurs without any manipulation or insertion of extra energy. The atomic positions so found at the reconstructed surface are output, not input. The only "bias" put in is that we "asked" for a 2x1 reconstruction by our initial choice of supercell. The reconstruction is spontaneous, and there is no barrier to the formation of the π-bonded surface. This agrees with the result of Northrup and Cohen [22] who find a very small barrier of 0.03 eV/surface atom between the Haneman and Pandey models. The energy difference between our initial and final states is 0.6 eV/surface atom. The energy difference (not the barrier) between the the

buckling model and the final state is about 0.2
eV/surface atom.

Si(001) Surface Reconstructions

The Si(001) reconstructed surface remains
incompletely understood. It seems relatively
clear that the c(4x2) reconstruction is the
ground state. Calculations [23] and experiment
(low temperature LEED [24]) agree on this point.
Less clear, but also indicated by calculations
[23][25], the p(2x2) reconstruction is lower in
energy than any 2x1 reconstruction.

For 2x1 reconstructions, the most recent self-
consistent LDA calculations [25][26] find that
the symmetric dimer is lower in energy than the
asymmetric dimer. The energy difference is
small, about 0.02 eV/dimer. However, the latest
self-consistent LDA band structure calculations
[23] give both the symmetric dimer and the
asymmetric dimer to be metallic; while,
experimentally, the surface is found to be
semiconducting [27]. Artacho and Yndurain [28]
have proposed that there is a strong spin
correlation within the dimer which would make
the symmetric dimer surface semiconducting, but
as yet the magnetic nature of the surface has
not been confirmed.

Room temperature STM images of the Si(001)
surface [24] show the p(2x2) and c(4x2)
reconstructions appearing principally near large
defects. In nominally clean regions of the
surface, the reconstruction is principally 2x1,
and the dimers appear to be symmetric. To sum
up, there is still a significant gap between
theory and experiment for the Si(001) surface.

The starting point for our simulation of the
reconstruction is the ideal terminated bulk
Si(001) surface (five atomic layers deep) in a
2x1 unit cell. (We have repeated the calculation
in a cell 13 layers deep with identical
results.) Dynamical quenching leads to a final
state of an asymmetric dimer. The symmetric
dimer is an intermediate state in this process.
The energies of these two states with respect to
the terminated bulk are: symmetric dimer, -1.65
eV/dimer, and asymmetric dimer, -2.26 eV/dimer.
We find the symmetric dimer surface to be
metallic and the asymmetric dimer surface to be
semiconducting. When relaxation is allowed in a
2x2 unit cell (two dimers in the same row), a
p(2x2) reconstruction is found, and for a 4x2
unit cell (two rows of two dimers each), a
c(4x2) reconstruction is found. The energies of
the p(2x2) and c(4x2) reconstructions with
respect to the terminated bulk are the same,
-2.33 eV/dimer.

We have also done simulations with steps
(described elsewhere in this paper) and
vacancies on the Si(001) surface and we have
found that the local environment is highly
influential in determining the symmetry or
asymmetry of dimers. For example, we find that,
for a surface with 25% defects (one dimer
missing out of a row of four), the dimers tend
to be symmetric. (Our result is similar to
Pandey's π-bonded defect model [26].) Work with
lower concentrations of defects and defects of
various shape and size is in progress.

VI. Interaction between a Si(001) Surface and an STM tip

Because of the importance of the STM in
determining the structure of the Si(001)
surface, we investigated the possible effects of
STM imaging on the Si(001) dimer reconstruction.
Demuth et al. [29] have suggested that the high
resolution of images of the Si(001) surface
might be due to tunneling between the surface
and Si clusters adsorbed on the STM tip. In view
of this, we created an STM tip made of four Si
atoms. Three of these atoms were fixed in an
equilateral triangle 3.84Å on a side in a plane
parallel to the surface. The fourth atom was
placed on the normal through the center of that
triangle and was free to move. This free tip
atom was relaxed and was placed above an
asymmetric dimer in a 2x2 unit cell. In this
simulation there was no potential difference
between the tip and the surface and there was no
tunneling current.

We began with the tip above the lower, or
"down", atom of the asymmetric dimer. We find
that, for an initial separation of 4.1Å or less,
the attraction between the tip and the surface
is strong enough to alter the tilt of the dimer
(Figure 4). In fact, the "down" atom is
attracted upward to a nearly symmetric position.
However, when the tip is moved directly above
the higher atom of the same asymmetric dimer,
the position of that atom is not significantly
affected. As a result, due to the STM tip-
surface interaction, an asymmetric dimer imaged
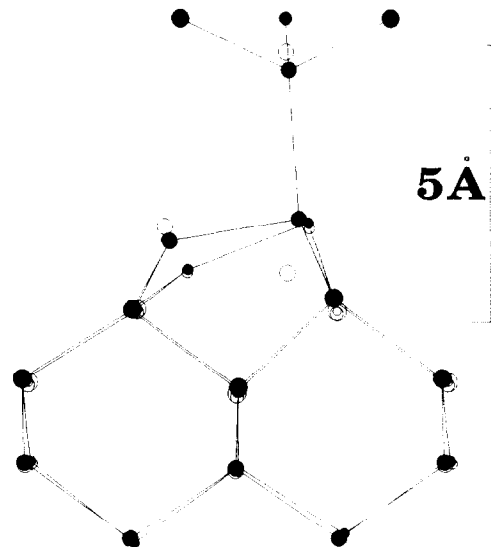by our STM tip would appear symmetric. Since the

Figure 4. STM tip interaction with Si(001)
asymmetric dimer in a p(2x2) unit cell. The
initial positions are the open circles, and the
final positions are the filled circles. The tip
is over the lower atom of the dimer. Initially,
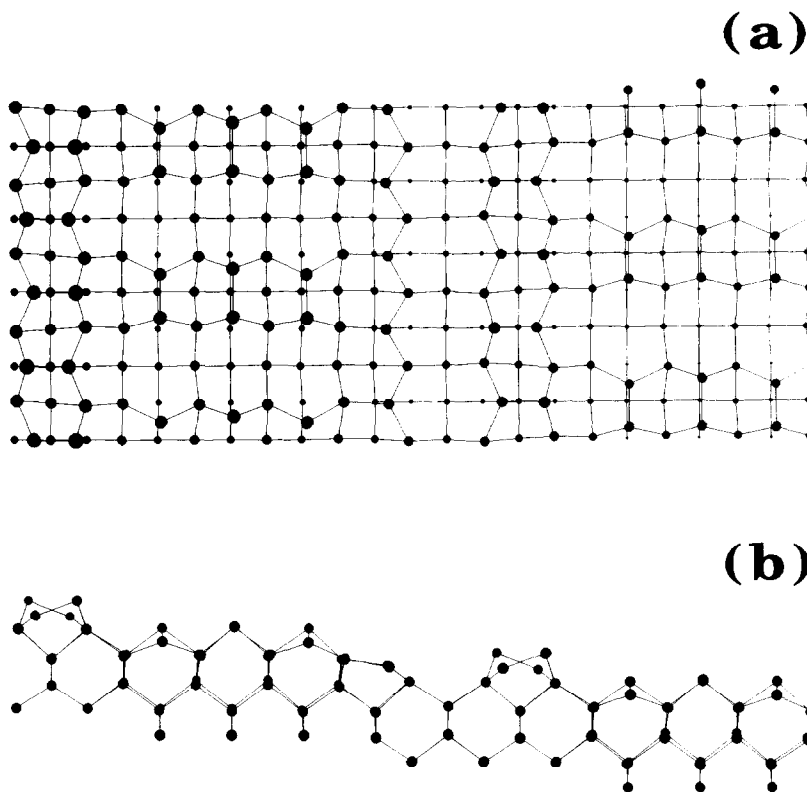the tip-surface atom separation was 4.0Å.

(a)

(b)

Figure 5. Simulated Si(001) vicinal surface with
smooth sB edge (a) Top view (b) Side view.

Si wavefunctions in our simulations vanish at r_c (2.645Å), 4.1Å should be regarded as a minimum cutoff value for this type of interaction.

VII. Kinked sB steps on the Si(001) Surface

The geometry of the Si(001) surface is such that, where single steps occur, dimers on the two levels run in perpendicular directions. When the dimer rows in the upper level are parallel to the step edge the step is named sA, following Chadi [30]. When the dimer rows in the upper level are perpendicular to the step edge the step is named sB. It has been experimentally observed [31] that sA steps tend to be straight or smooth, while sB steps tend to be kinked or jagged.

As a first step in understanding the origin of the jagged step, we have compared the total energies of fully atomically relaxed sB kinked and straight steps. We elected to use a vicinal (1,1,13) surface with a tilt angle of 6.2 degrees. The steps were modeled according to Chadi [30]. We began with a 64 atom supercell using symmetric dimers and then allowed the

system to relax into asymmetric dimers (Figure 5). The three dimers atop the sB step were found to form a pattern in which the outer two dimers were asymmetric while the central dimer was nearly symmetric. The 64 atom cell was then repeated along the step, doubling the size of the unit cell. We again allowed this system to relax and found a negligible change in the final energy, as expected. This was taken as the energy of a smooth sB step.

To create a kinked sB step, a single dimer from one row of three was removed and placed at the head of the second row of three dimers, creating a row of two dimers and a row of four dimers. This 128 atom system was then dynamically quenched to find the ground state. The final energy of the kinked edge is 0.04 eV/a (a = 3.84 Å along the step edge) lower than that of the smooth sB edge.

There was considerable geometrical relaxation within the dimer row containing four dimers. In particular, the dimer which had been symmetric (the dimer at the center of the old row of three) became asymmetric, while the added dimer relaxed to a symmetric configuration (Figure 6).
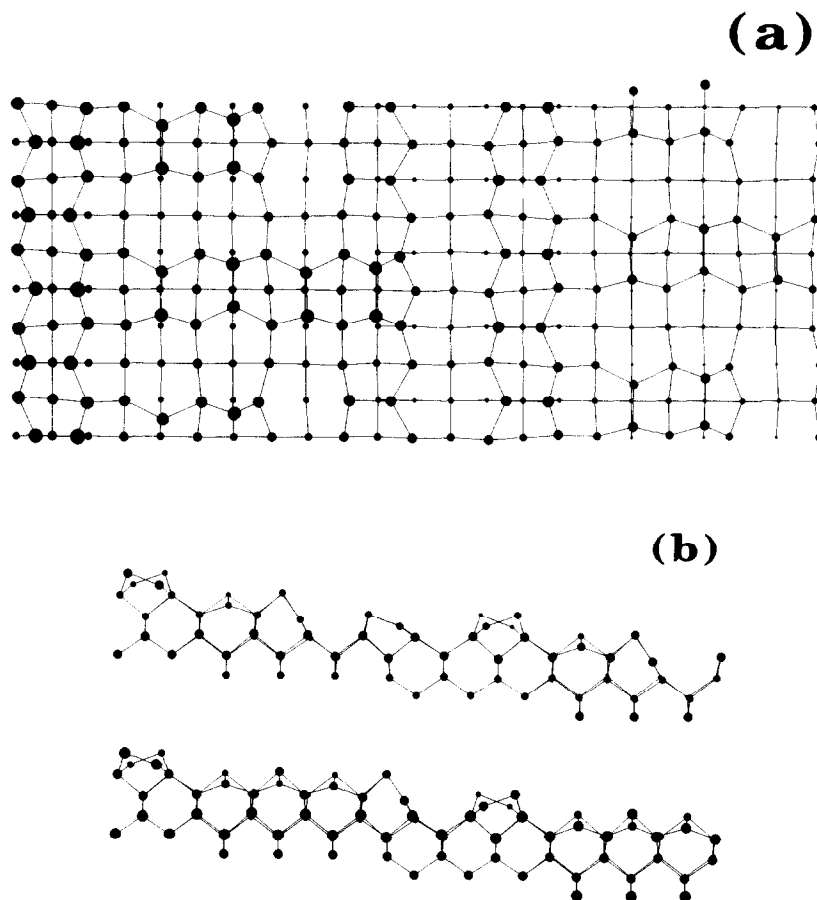
(a)

(b)

Figure 6. Simulated Si(001) vicinal surface with
kinked sB edge (a) Top view (b) Side views.
Upper drawing shows rows of two dimers. Lower
drawing shows rows of four dimers.

There was also considerable relaxation of second
layer atoms at the newly formed step edges.
   These results suggest that the kinked sB step
is lower in energy than the smooth sB step.
However, in interpreting this result one must
consider that there are two types of sB step
edges. In one type, the sB edge connects to the
side of a dimer row in the lower level. Chadi
[30] refers to this edge as a rebonded sB edge.
In the other type, the sB edge connects to the
side of a trough (like those between dimer rows)
in the lower level. Chadi [30] refers to this as
a nonbonded sB edge. Removing or adding a single
dimer to a dimer row at an sB edge changes the
sB edge type. For example, in this calculation,
we have changed from rebonded sB edges (in our
smooth sB edge) to nonbonded sB edges (in our
kinked sB edge). To complete our study of this
type of kink we must also begin with a smooth,
nonbonded sB edge, and end with a kinked,
rebonded sB edge. This calculation and other
work with kinked sB steps is in progress.

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