

Surface Relaxations, Current Enhancements, and Absolute Distances in High Resolution Scanning Tunneling Microscopy

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We have performed the most realistic simulation to date of the operation of a scanning tunneling microscope. Probe-sample distances from beyond tunneling to actual surface contact are covered. We simultaneously calculate forces, atomic displacements, and tunneling currents, allowing quantitative comparison with experimental values. A distance regime below which the probe becomes unstable is identified. It is shown that the real distance differs substantially from previous estimates because of large atomic displacements on the surface and at the probe tip.

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It is hard to avoid the scanning tunneling microscope (STM) in the imaging, fabrication, or characterization of nanoscale structures today [1–6]. It is certainly the most ubiquitous tool in surface science. But while the formation of atomic wires from metal leads and their final breaking is well researched [3,4], the physics of the reverse process—an STM tip approaching the surface at very close range—is far less documented. Even more importantly, several routes are currently being explored to fabricate and operate electronic devices on the nanoscale [7–9]. In chemical methods of nanofabrication [9] a high precision of atomic assembly is attainable, even though the exact position of every atom is not controlled. By contrast, to initiate such a process, or to craft structures by moving each element into place, the exact position of the STM tip and the target atoms must be known. Furthermore, nanoscale research requires a high degree of knowledge about the electronic, chemical, and transport properties of potential constituents—information often obtained by STM. This information may be misleading if the tip-sample distance is not correctly estimated. Therefore, as soon as the work moves from qualitative to quantitative, distance estimates are of critical importance. The question of distances was previously analyzed to some extent for STM [2–5], and for the related scanning force microscope [10–12]. What is missing, so far, is a picture of the interplay between forces, relaxations, and currents.

In this paper we analyze the interactions between tip and sample and their effect on distance estimates and STM images from first principles. We demonstrate that our simulation technique allows us to keep track of all key quantities in this situation. We chose the Au(111) surface since it is widely used in nanotechnology and was studied in recent extensive experiments [13,14].

The computational method is based on first principles density functional theory. We employ periodic boundary conditions both parallel and perpendicular to the surface. The sample surface was mimicked by a five layer Au(111) film with nine atoms per layer. The high number of atoms per layer was necessary for a complete decoupling of the interactions between adjacent tip pyramids. The central layer of the Au(111) film was our plane of reference. The tip apex was mimicked by a tungsten tetrahedron mounted on the reverse of the Au(111) surface slab; the tip-sample separation was altered by varying the size of our unit cell normal to the surface. Tungsten is the most commonly used tip material in experiments; the low reactivity and the similar size of tungsten and gold atoms makes the support of the tip apex on gold realistic. We also checked its plausibility by a careful analysis of the forces during our simulations. In this case the force gradients are mainly due to the position of an atom, but not its chemical nature. In Fig. 1 we display the forces on the apex atom and the subsurface atoms of the tip, it can be seen that the forces on the apex atom are about 1 order of magnitude higher.

Even for the pseudopotential Vienna *ab initio* simulation program [15,16] code the simulations were rather demanding and at the limit of realistic time scales. This fact ruled out a check of the results including additional gold or tungsten layers. For the same reason we did not include long-range forces. But, as established by Perez *et al.* in their analysis of atomic force microscopy [11], they only cause significant relaxations in the very low distance regime (below 5 Å), and in this range short-range forces are substantially higher, as we find in our simulations. The same point was made in an earlier publication by Dürig *et al.* [17]. We also neglect bias-induced surface relaxations in our treatment. The technical details of the calculation are the following: The cutoff of the ultrasoft

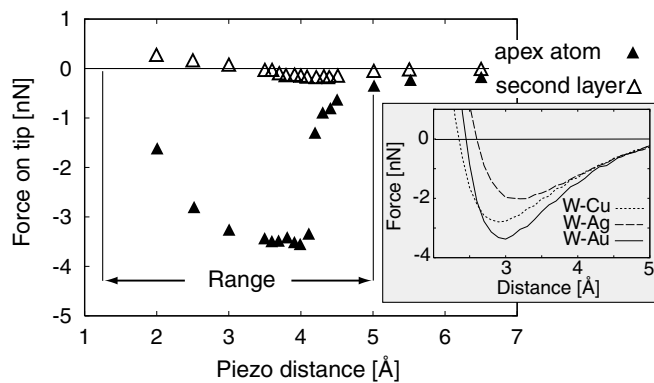


FIG. 1. Forces on the apex atom (full triangles) and the subsurface atoms (empty triangles) of the tip above the hollow position of the Au(111) surface. The forces on the apex atom are about 1 order of magnitude higher. The range of forces is about 4 Å. Inset: forces on Cu, Ag, and Au atoms in a dimer. The forces between the tungsten atom and the noble metal atom are roughly equal in a distance range above 4 Å.

pseudopotentials [18] was 230 eV, exchange and correlation effects were computed with generalized gradient correction and by using the formulation of Perdew *et al.* [19]. The Brillouin zone was sampled with $(4 \times 4 \times 1)$ k points of a Monkhorst-Pack grid [20]; forces were converged to values of less than 0.01 eV/Å.

The reading of a piezoscale in the experiments is given by the position of the plane of reference in the supercell setup of our system. From an initial tip-sample separation of 10 Å the distance was gradually reduced, initially in steps of 0.5 Å. At every step the system was fully relaxed. The onset of significant mechanical interactions between tip and sample occurs at about 5.0 Å. To determine the precise effect of these interactions in the low distance range we reduced the distance in steps of 0.1 Å from 5.0 to 4.0 Å for one tip position (STM tip on top of a surface atom), and from 4.5 to 3.5 Å for the second tip position (STM tip between the surface atoms). We computed the surface wave functions for the fully relaxed sample and tip systems at every distance and for two tip positions. In this part of the calculation the initial system was separated into two subsystems, the sample and the tip surface, and the surface wave functions computed for each subsystem separately. These wave functions were used as the input for our simulation of the tunnel currents [21]. The procedure leads to separate constant-current contours of the surface, depending on the position of the tip. Interpolating between the two simulations we obtain the change of corrugation due to system relaxations from first principles.

It has been shown by a number of authors [2,5,11] that substantial relaxations are confined to the low distance regime. Perez *et al.* obtained their result with an *ab initio* method, but they calculated the changes on a semiconductor surface and did not relate them to measured currents. Olesen *et al.* [5] and Clarke *et al.* [2] analyzed the events on metal surfaces, but employed empirical potentials; for this reason they, too, could not simultaneously

evaluate the current. Their results show, not surprisingly, that the onset of forces and relaxations begins when the interatomic distances are close to the typical bond length of the atoms. However, from experiments we know that tip-sample forces on Au(111) are appreciable for distances of at least 5 Å [13,22]. Di Ventura and Pantelides employed density functional theory to determine the relaxation of surface atoms for Al(110) surfaces, mimicking the tip by a single Al atom [23]. Within the range of distances from the point contact to the tunneling regime (1.3 to 3.3 Å) they predict no corrugation due to atomic relaxations. The present calculation is in a sense complementary to their work. It is shown here that experimental conditions in STM scans do not allow such a close approach, because the system already becomes unstable at larger distances (4.6 Å). Our calculations establish an early onset of relaxations, which depend strongly on the position of the tip. For the on-top position of the STM tip we observe an onset of forces and relaxations at about 4.7 Å, about 1.0 Å higher than suggested by earlier simulations [2,5]. The surface atom reaches its farthest elongation from the surface at a tip-sample separation of 4.5 Å; it is then 1.3 Å above its position on the isolated surface. This point marks the beginning of atomic transfer from the surface to the tip, the origin of the hysteresis observed in single approach/retraction cycles [3]. Neighboring atoms on the surface are equally relaxed, their maximum displacement is 0.1 Å. The second nearest neighbors remain close to their original position (vertical displacement less than 0.04 Å). Even though the boundary conditions at our two-dimensional repeat unit constrain the relaxations of individual atoms, the very small relaxation of second nearest neighbors indicates a rapid decay of the forces in the lateral direction. Therefore we do not expect substantial changes in a calculation performed with a larger unit cell. If the tip is in the three-fold hollow, the onset of forces and relaxations is substantially retarded and occurs at 4.3 Å. The maximum outward relaxation of the three gold atoms is somewhat lower and about 1.0 Å (reached when the tip-sample separation is 4.1 Å).

The tungsten tetrahedron of the STM tip relaxes about the same amount in both positions: The apex atom approaches the sample by about 0.5 Å at the point of closest approach. The change is due to an increase of the interlayer distance of the tungsten atoms by about 0.1 to 0.2 Å, and a buckling of the layers underneath, which extends about two layers into the lead. The forces on the tungsten tip are shown in Fig. 1. The values for tip-sample relaxations are given in Fig. 2. Owing to the strong interactions between tip and sample at close range, the core-core distance between tip and sample is decreased. The net effect of relaxations is a decrease of the distance between tip and sample. A deviation of about 2 Å between the distance inferred from simulations, and the distance inferred from measurements of the decay, has actually been observed [24]. In the critical range of 4.6 to 4.1 Å the actual distance changes by about 2 Å. The real distances are shown

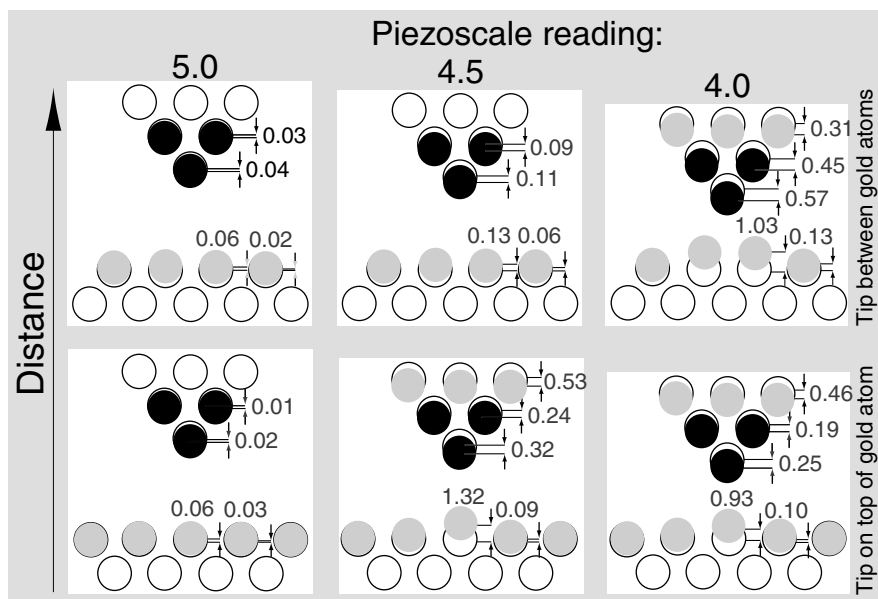


FIG. 2. Relaxed positions of sample and tip atoms for three piezoscale readings of the STM: 5.0 Å (left), 4.5 Å (center), 4.0 Å (right); also two STM tip positions. At the point of closest approach the closest Au surface atoms are about 1 Å higher than on the isolated surface. Note that relaxations differ substantially for the two different positions.

in Fig. 3(a). This points to an effect frequently observed in experiments with atomic resolution: It is difficult to obtain atomically resolved images, because sizable corrugations in most cases require a distance below 5 Å, but it is very easy to destroy an STM tip by small increases of the current. We now understand that the actual range of imaging is less than 1.0 Å, or less than an order of magnitude in the current scale. Stability is destroyed, when the apex atom of the tip and an atom of the sample form a chemical bond. To check whether a different metal surface would lead to different results and thus a different interval in actual measurements we computed the forces between a tungsten atom and a Cu, Ag, and Au atom in a dimer configuration. The result of our calculation is shown in the inset of Fig. 1. It can be seen that the forces are equal

for all three noble metals in the range above 4 Å. Short of performing identical simulations for all three surfaces this seems the best confirmation that our result is of general validity.

Currents were calculated in a perturbation approach [21] and based on the fully relaxed sample and tip systems. The current was calculated for a sample bias of -0.1 V. The curves in Fig. 3(b) show the current for the hollow position. We obtained the change due to surface and tip relaxations by calculating the full range of currents in a frozen atomic configuration. The logarithmic graphs are different for every distance, the z labels give the tip-sample separation before relaxation. The true increase of the current is determined by taking only a single point of each graph. In practice we interpolated between the computed points to obtain the smooth black curve shown in the figure, giving an enhanced increase in the current. For an experimenter who estimates the potential barrier between tip and sample from the exponential decay of the current, the apparent barrier height increases in this range [17,25]. The current calculation is based on the Bardeen approach [26], where sample and tip are considered decoupled. In a previous paper we studied the effects of a tip potential on the surface electronic structure [24], and it was established that these effects are limited to very low distances (below 4 Å). Here we find that the onset of relaxations begins about 1 Å before this point. The main effect, not included in perturbation theory, is therefore due to relaxations. But this indicates that a more refined treatment of STM currents, e.g., by a scattering approach, is no substantial improvement compared to the Bardeen approximation, if it does not simultaneously treat relaxations. And this, in turn, is still computationally untractable because it requires a fully *ab initio* treatment for every single position of the tip.

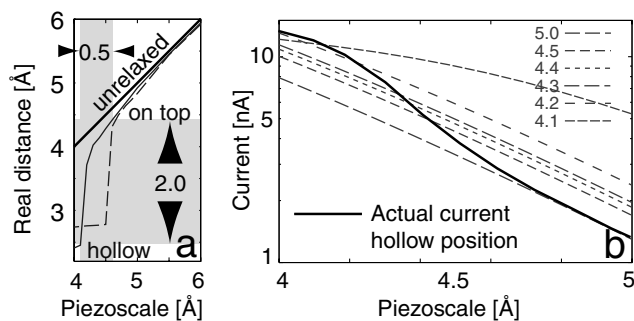


FIG. 3. Relaxations and currents of the coupled system. The separation decreases, within a distance of 0.5 Å, by as much as 2.0 Å (a). Logarithmic current graphs computed from the wave functions of the relaxed system. Individual curves pertain to equilibrium positions at a specific piezoscale reading. In the range of measurements at about 4.5–5.0 Å the current decays faster due to relaxation effects, the actual barrier height seems to be increased (b).

All the results presented here are derived from *ab initio* treatments of currents and relaxations for two lateral positions of the tip: the on-top position and the threefold hollow. The tunnel currents in our simulations were assumed to be 5.1 nA in both cases, but owing to the site-dependent relaxation of the systems the two constant-current contours differ. The piezoscale would give a distance of 4.7 Å on top of a gold atom and 4.5 Å in the fcc hollow site. These distances are at the lowest limit of stability for the tip-sample system. The difference of 0.2 Å describes the experimental corrugation of the Au(111) surface, when measured with a tungsten terminated tip [6]. The simulated scans with the tips and surfaces frozen in the two relaxed configurations are shown in Figs. 4(a), and 4(b). We stress that these images are idealizations, because they were computed with the wave functions of frozen atomic positions of tip and sample. In Fig. 4(c) we show two simulated line scans across a single atom. The two separate curves describe the line scan for the two setups used (on-top and hollow). It can be seen that the relaxation leads, in effect, to an enhancement of the corrugation by about 0.13 Å. Only with this relaxation do we obtain agreement between experiments and simulations [6].

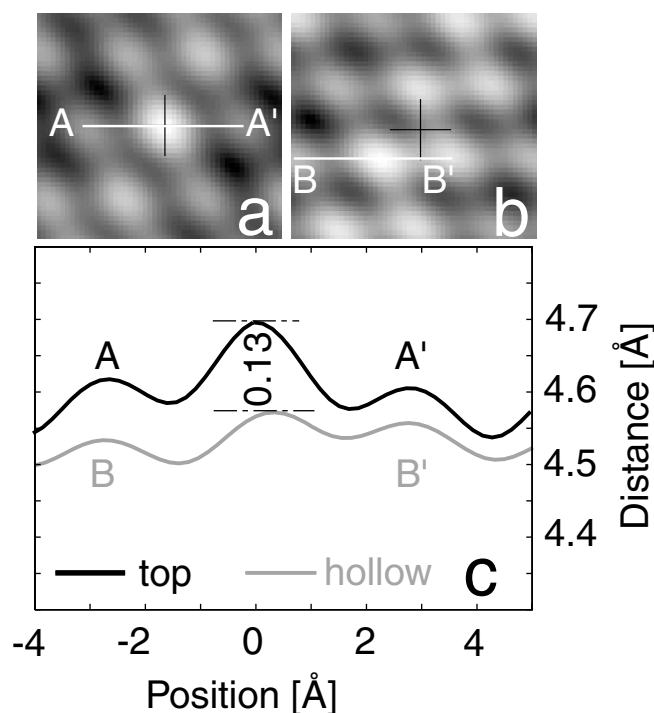


FIG. 4. Current contour plots using the relaxed configurations of sample and tip for a distance of 4.7 Å [tip on top of an Au atom, frame (a)], and 4.5 Å [tip in the threefold hollow position, frame (b)]. Simulated line scan across a single atom (c), for the setup in the on-top position [black curve, A-A' in frame (a)] and for the setup in the hollow position [grey curve, B-B' in frame (b)]. All scans correspond to a current of 5.1 nA. An actual scan would have enhanced corrugation due to relaxation effects [see dash-dotted lines in frame (c)].

The most remarkable result of our calculations, and the one that experimenters may find most important, is the very low range of stability for atomically resolved STM scans on metal surfaces. This range is only about 0.5 Å. Below this point, at about 4.5 Å from the surface, the distance between tip and sample changes drastically by 2 Å (within 0.5 Å of measured displacement), as the two separate systems jump into contact. In this range the current may even decrease as the tip approaches, if one atom of the tip or sample system becomes separated.

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