Ab initio calculations of scanning tunneling microscopy images within a scattering formalism

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I. INTRODUCTION

The scanning tunneling microscope (STM) is a very powerful tool to study surfaces and elementary processes of adsorbates on surfaces. The estimation of the electronic current between a sharp tip and a surface provides a local imaging technique at the atomic scale. By changing the bias voltage between the tip and surface, this technique opens up a wide field of local spectroscopy. Even though it has been mainly used in the past for semiconductors, scanning tunneling spectroscopy is now widely applied to metal surfaces and adsorbates.1–5

However, the technique does not give a direct image of the atoms, but rather probes its electronic structure close to the Fermi level. Therefore, one crucial issue is the accurate interpretation of the images. A striking example is graphite, where generally only half of the surface atoms are seen in the images.6 The shape of the image is not directly related to the atomic positions at the surface, as the tip Z position in the image does not correspond to the Z coordinates of the atoms. For example, an oxygen atom adsorbed on a metal surface is seen as a depression in the STM image.7 Thus theoretical calculations of the tunnel current and the STM images are clearly needed to understand these images fully, and to obtain a better interpretation of the observed contrast. Accurate calculations could become a reliable tool to determine the surface structure with STM by an adequate fit to the experimental data.8

There are clearly two steps in a theoretical calculation of the STM current between a tip and a surface. The first one is the determination of the electronic structure of the system which can be obtained at any levels of approximation: tight-binding methods, jellium models, or different types of first-principles calculations. The second is the calculation of the STM current itself. Various levels of approximation can be used. The most popular one relies on Bardeen’s perturbation theory,9 and was formulated by Tersoff and Hamman.10 In this approach, the tip is modeled by an s wave, whereas the tunnel current is proportional to the local density of states at the Fermi level energy and evaluated at the tip center of curvature. The second class of methods is based on multiple-scattering formalisms which go beyond perturbation theory and provide a full description of the interactions between the substrate and the tip (i.e., they include all tunneling events). This approach has been mainly applied in conjunction with semiempirical descriptions of the wave functions,11,12 but only a few STM studies combine a first-principles treatment of the Hamiltonian and a scattering formalism for the current.

Among others, Hirose and Tsukada developed a method where scattering waves are calculated by a step-by-step recursion matrix technique.13 The system is composed of two parallel semi-infinite jellium electrodes with several atomic layers attached to them. The electronic structure is determined self-consistently. Hirose and Tsukada applied this method to study the atom extraction by STM. Doyen, Drafkova and Scheffler developed a Green’s-function theory of STM.14 The sample in the calculations is a semi-infinite crystal built from muffin-tin potentials. The tip base is represented by a free-electron metal with one adsorbed atom for the tip apex. The scattered wave function is calculated within the single-particle approach using a Green’s-function tech-
reservoirs characterized by chemical potentials $\mu_S$ and $\mu_T$, respectively. The difference between the two chemical potentials is controlled by an external bias $V$ applied between $S$ and $T$, so that $\mu_T - \mu_S = eV$ (with $e < 0$). The tunneling region is made of the tip apex $A$, the surface with adsorbates $R$, and the vacuum. It is embedded between $S$ and $T$. For $V > 0$, the electrons propagating from $S$ to $T$ first reach the tunnel gap regarded as a defect within the periodic structure of $S$ and are then scattered. The measured tunneling current is given by the small fraction of these electrons which reach $T$ and couple to states propagating away from the junction. The tunnel process is therefore considered as a scattering mechanism for which the scattering matrix $S$ is calculated from the electronic transmission and reflection amplitudes at the tunnel junction. The conductance is then evaluated via the Landauer-Büttiker formula for the multichannel case.\(^{17}\)

At the zero-temperature limit, the current $I$ is

$$ I(V) = \frac{e^2}{\pi h} \int_0^{-eV} T^{\pm}(E + \mu_T) dE. \quad (1) $$

The total transmission coefficient $T^{\pm}(E)$ is

$$ T^{\pm}(E) = \sum_{m,m'} T^{\pm}_{mm'}(E), \quad (2) $$

where the matrix elements $T^{\pm}_{mm'}(E)$ give the probability for an electron in channel $m$ at the negative side of the tunnel junction to be transmitted into channel $m'$ at the positive side. The channels are the asymptotic solutions far from the junction. Therefore, they are the Bloch wave functions at the considered energy for the surface and tip bulk systems. For $V > 0$, $(\pm)$ indicates that the electrons propagate from $S$ to $T$, whereas $(\mp)$, indicates propagation from $T$ to $S$. The transmission coefficient $T^{\pm}_{mm'}(E)$ can be directly extracted from the scattering matrix elements $S_{mm'}(E)$ through

$$ T^{\pm}_{mm'}(E) = |S_{mm'}(E)|^2 \frac{\nu_m}{\nu_{m'}}, \quad (3) $$

where $\nu_m$ ($\nu_{m'}$) is the group velocity of channel $m$ ($m'$).

The tunnel junction is modeled in the following way. First, the bulks of the substrate $S$ and the tip $T$ are described by the periodic repetition of identical block $s_1$ ($t_1$). The $r$ block corresponds to the surface block and $a$ is for the apex block.

### II. SCATTERING FORMALISM

As depicted in Fig. 1(a), the STM experimental setup is modeled by two semi-infinite metallic wires corresponding to the substrate $S$ and the tip $T$, each connected to electron reservoirs characterized by chemical potentials $\mu_S$ and $\mu_T$, respectively. The difference between the two chemical potentials is controlled by an external bias $V$ applied between $S$ and $T$, so that $\mu_T - \mu_S = eV$ (with $e < 0$). The tunneling region is made of the tip apex $A$, the surface with adsorbates $R$, and the vacuum. It is embedded between $S$ and $T$. For $V > 0$, the electrons propagating from $S$ to $T$ first reach the tunnel gap regarded as a defect within the periodic structure of $S$ and are then scattered. The measured tunneling current is given by the small fraction of these electrons which reach $T$ and couple to states propagating away from the junction. The tunnel process is therefore considered as a scattering mechanism for which the scattering matrix $S$ is calculated from the electronic transmission and reflection amplitudes at the tunnel junction. The conductance is then evaluated via the Landauer-Büttiker formula for the multichannel case.\(^{17}\)

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The tunnel junction is modeled in the following way. First, the bulks of the substrate $S$ and the tip $T$ are described by the periodic repetition of blocks along the Z direction as shown in Fig. 1(b). These blocks are denoted by principal layers (PL’s), which are composed of several atomic planes and are periodic in the lateral directions X and Y. To model this lateral periodicity, we consider a supercell made of several blocks and apply periodic boundary conditions. The PL’s belonging to the bulk block $S$ ($T$) are called $s$ ($t$). The surface $R$ and apex $A$ are each modeled by a single PL denoted by $r$ and $a$, respectively.

A set of atomic orbitals (AO’s) is associated with each atom of the different PL’s and the wave function at each PL is expanded within the linear combination of atomic orbitals framework. The valence AO’s are commonly used for the scattering matrix calculation. In the model, we only consider interactions between first-nearest-neighbor PL’s. The number of atomic planes per PL can be chosen in order to limit the influence of this approximation.
Several types of Hamiltonians (H) can be employed. Semiempirical methods like the extended Hückel theory were used in the past, since they provide qualitatively reliable and fast calculations. Here the Hamiltonian matrix elements are calculated from a first-principles DFT approach to obtain a more accurate description of the electronic structure.

Once the matrix elements of the Hamiltonian (H) and the overlap (O) were obtained for the selected AO basis set, two methods were employed to evaluate the scattering matrix S. One is known as the electron-scattering quantum-chemistry method (ESQC).\(^{11}\) The second is based on Green’s-function techniques.\(^{12}\)

Within the ESQC method, S is calculated via the transfer matrix (TM) technique, which connects the propagating wave amplitudes at the sample side of the junction to the tip side. The TM is evaluated via the use of spatial propagators in the bulk and across the junction. This technique requires two identical wires S and T, that is to say, their geometry and their electronic structure must be identical. Consequently, no finite bias can be applied between S and T, and a true spectroscopic analysis is not possible. The conductance is always evaluated in the zero-bias limit. Although this technique is remarkably fast, it is not very numerically stable due to the inversion of off-diagonal matrices required to build up the propagators. A small energy shift (between \(10^{-6}\) and \(10^{-10}\) eV) is often added to these matrix elements to stabilize the ESQC procedure.

Alternatively, S can be obtained via the use of Green’s functions. After calculating the channels for the bulk of the sample and the tip, the Bloch states are coupled to their respective surfaces. In other words, channels at S are coupled to the R block, and channels at T are coupled to the A block. This coupling is done via renormalized transfer matrices \(T_{ra}\), \(T_{ar}\), or \(T_{sr}\) and \(T_{sr}\) or \(T_{ra}\) depending on the direction of the electron propagation. These matrices are obtained through Green’s-function techniques. They relate the amplitude of the channel at the bulk with the amplitudes of the AO’s at the surface. The AO’s at R and A are connected by the interface Green’s-function matrices \(G_{rr}\) and \(G_{aa}\). The latters are exactly obtained within the surface Green’s-function matching framework, or approximated to first order in the number of tunneling events by using the first terms in the expansion of the Dyson equation. Finally, \(S(E)\) takes the simple form

\[
S(E) = T_{sr} G_{ra} T_{ar} \quad \text{if} \quad V < 0,
\]

\[
S(E) = T_{ra} G_{ar} T_{rs} \quad \text{if} \quad V > 0.
\]

In this method, different S and T bulk blocks are allowed. S and T may have different chemical natures, and a finite voltage may be applied. Thus spectroscopic data can readily be obtained. A small imaginary part is added to the energy \(E\) of the propagating electrons in order to avoid divergences when evaluating the Green’s functions. The formalism is numerically stable for an imaginary part as low as \(10^{-6}\) eV. Large imaginary parts of the energy result in a shorter decay of the wave functions, which may be considered as a crude approximation to the inelastic scattering effects.

The first-order approximation is very useful in order to perform an analysis of the current in terms of AO contributions. In this case we have

\[
G_{ar}^{1} = G_{ar}^{0} F_{ar} C_{rr}^{0},
\]

where \(G_{ar}^{1}\) is the first-order Green’s function linking a and r. \(G_{ar}^{0}\) and \(G_{rr}^{0}\) correspond to the Green’s functions at the surface blocks when the two wires are completely decoupled. \(F\) is the matrix defined as \(E \times O - H\). All the details for these equations are described in Ref. 12.

Within the first-order approximation, the total transmission coefficient \(T\) can be decomposed through

\[
T^\pm(E) = \sum_{r, a_j} T^\pm_{ra}(r_j, a_j, E).
\]

\(T^\pm_{ra}(r_j, a_j, E)\) gives the contribution to the total transmission coefficient arising from an electron that has tunneled from the AO \(r_j\) at R to the AO \(a_j\) at A for \(V > 0\), and vice versa for \(V < 0\). This coefficient may be either positive or negative due to electronic interferences effects. A negative value means a net destructive interference. Although the \(T^\pm_{ra}(r_j, a_j, E)\) quantities might be positive or negative, the total sum over AO’s at R and A will always be positive. The sum over all the propagating channels \(mm'\) has been included in the \(T^\pm_{ra}(r_j, a_j, E)\) coefficient.

### III. AB INITIO STM CALCULATIONS

#### A. ADF-BAND program

The self-consistent Hamiltonian was calculated with the ADF-BAND program.\(^{19}\) This code is well adapted to periodic systems and uses a localized orbitals basis set. The program is based on the functional theory DFT within the Kohn-Sham approach. Calculations can either be performed at the local-density-approximation (LDA) level, or at the generalized-gradient-approximation (GGA) level.

The code uses flexible basis sets consisting of numerical atomic orbitals (NAO’s) and Slater-type orbitals (STO’s). The NAO’s correspond to the numerical solution of the DFT equations for the free atom. k-adapted Bloch functions are constructed from the one-center functions (NAO’s and STO’s). The frozen-core approximation can be used for the inner core atomic states. The valence basis is orthogonalized with respect to the frozen-core states.

The Coulomb potential is evaluated via an expansion of the charge density in suitable function sets. The density fitting procedure is the following: a set of Slater-type fit functions is used for each atom, and the electronic density is expanded on this basis.

\(k\)-space integration is performed by applying the quadratic tetrahedron algorithm to a \(k\) mesh centered at the \(\Gamma\) point. For \(1 \times 1\) unit cells, a mesh consisting of \(N_{DFT}^{k} = 16\) \(k\) points usually gives reasonable results, while \(N_{DFT}^{k} = 64\) provides very well-converged results in most cases.

As for the matrix elements of H and all real-space integrations, a Gauss-type numerical integration method is used. The precision of these integrals is typically set to yield relative errors \(< 10^{-4}\).

#### B. Implementation of a self-consistent Hamiltonian

Given a set of AO’s, the Hamiltonian and overlap matrix elements must be evaluated on each PL and between two
consecutive PL’s in order to calculate the tunneling current. That is to say, \( H_{ij}, H_{ij+1}, H_{r}, H_{ar}, H_{ta}, H_{at}, H_{fr}, \) and \( H_{fr+1} \) must be determined and so do the \( O \) matrix elements [see Fig. 1(b)].

The whole system being infinite in \( Z \), DFT calculations are performed on fragments of the system which are modeled by finite slabs. These fragments must simulate the different blocks \( s, t, r, \) and \( a \), and must take into account the various chemical environments of these blocks. The technique adopted is the following.

1. We perform a DFT calculation on the simplest fragment to model the chemical environment of the atoms that are to be described. For instance, for the \( H_{s}, O_{s} \) matrices, the slab to be considered contains the \( r \) layer, the upper \( s_{1} \) layer, and also the \( s_{2} \) layer in order to have a correct environment for all the atoms in layer \( s_{1} \). The periodicity of the fragment in the \( XY \) plane is set equal to that of the blocks we are modeling. Obviously, for matrices involving bulk-type blocks, the periodicity may be set to \( 1 \times 1 \). Otherwise, the periodicity will be determined by the superlattice present at blocks \( r \) or \( a \). The \( O \) and \( H_{k} \) matrix elements are then obtained from the fragments calculations. In the following section, the extraction of these \( k \) matrices will be better explained with several examples.

2. Since the \( abf-band \) program makes use of the symmetry of the system by only including in the calculation those \( k \) points contained in the irreducible Brillouin zone (BZ), the \( H \) and \( O \) \( k \) matrix need to be determined for all the other \( k \) points in the BZ. If \( H(\tilde{k}) \) is the calculated Hamiltonian matrix at \( \tilde{k} \), and if \( \tilde{k'} \) is another \( k \)-point symmetry equivalent to it, we then have
\[
H(\tilde{k'}) = U^\dagger H(\tilde{k}) U,
\]
and a similar relation for the \( O \) matrix. Here \( U \) is the symmetry operator that maps \( \tilde{k} \) into \( \tilde{k'} \), and takes into account the symmetry properties of each AO. \( U^\dagger \) is its adjoint. A phase factor must also be included if one atom is moved from the original cell to a neighboring one upon the symmetry operation.

3. The \( k \)-matrix elements are finally transformed into real space through the standard relation
\[
H(\tilde{R}) = \frac{1}{N_{k}^{DFT}} \sum_{\tilde{k}} e^{-i\tilde{k}\tilde{R}} H(\tilde{k}),
\]
where \( \tilde{R} \) is a vector belonging to the two-dimensional Bravais lattice of the periodic system and consistent with the Born-von Karman conditions employed to generate the \( k \) mesh. \( H(\tilde{R}) \) corresponds to the real-space Hamiltonian matrix defined by
\[
H_{ij}(\tilde{R}) = \langle i | H | j + \tilde{R} \rangle,
\]
where \( i \) and \( j \) represent AO’s of the original cell. Analogous relations hold for the overlap matrix elements, \( O_{ij}(\tilde{R}) \), in real space.

Since the \( k \) sampling for the DFT calculations is finite, the real-space matrix elements can only be calculated for a limited range of \( \tilde{R} \) vectors in the two dimensional Bravais lattice. \( H \) and \( O \) real matrix elements beyond that range have been set to zero. However, in the practical applications described below, this limited range of interactions is longer than the one arising from the nearest neighbor interaction between PL’s.

The real-space matrices are directly used in the ESQC or the Green’s-function program. In the latter, they will be back-transformed into reciprocal space, with the possibility of using a finer grid for the current calculation than the one selected in the DFT calculation of the electronic structure.

IV. APPLICATION TO THE CU(001) SYSTEM

A. Description

1. Model of the junction

The above combined method for the \( ab \) \textit{initio} simulation of STM images was applied to the clean Cu(001) surface. First, this system is modeled as depicted in Fig. 2, where a projection on a plane containing the \( Z \) and \( X \) directions is shown. The surface block \( r \), together with all PL’s at \( T \) and \( S \), consist of two Cu atomic planes oriented along the [001] direction. The block \( a \) for the apex is composed of one atomic plane of Cu with one Cu atom adsorbed in a hollow position below with a \( 2 \times 2 \) periodicity. Since the overall lateral periodicity of the system is \( 2 \times 2 \), the blocks \( s, t, \) and \( r \) each contain eight Cu atoms, while for \( a \) we have five atoms in the unit cell (see Fig. 2).
All the Cu-Cu distances are set to 2.507 Å, which is the LDA calculated optimal distance for the bulk Cu. The apex is first positioned on a hollow site, i.e., the last Cu atom at the apex is equidistant with four Cu atoms at the surface. It should be noted, that, in our model, the tip apex is periodically repeated. In our following calculations, the current was divided by the number of tip apex in the supercell in order to normalize it to one tip apex.

2. DFT calculated fragments

After modeling the system, we performed DFT calculations in order to obtain the H and O k matrix elements on different fragments which model the different blocks in their chemical environment. First, the matrix elements \( s_i s_{i+1}, \) \( t_i t_{i+1}, \) \( t_i t_{i+1} \) were obtained from a calculation for a XYZ-periodic bulk, and composed of eight Cu atomic planes oriented along the [001] direction. The lateral periodicity of this slab was reduced to \( 1 \times 1 \). Two consecutive planes represent a \( t_i \) or \( s_i \) block. The matrix elements \( s_i, s_{i+1} \) and \( t_i t_{i+1} \) were obtained considering the interactions between the blocks \( s_i \) or \( t_i \) and the two planes above. For the \( rr \) and \( rr \) matrix elements, we employed a slab with a 14 atomic layers thickness and a \( 1 \times 1 \) periodicity in the \( XY \) plane. The first two planes exposed to the vacuum region corresponded to the \( r \) block, and the two planes below to the \( s \) block. For the \( rr \) tip-surface matrix elements, we defined a slab with a \( 2 \times 2 \) periodicity in the \( X \) and \( Y \) directions and composed of two blocks separated by a distance \( z \); the surface block \( r \) contains two Cu atomic planes (see Fig. 2), while the tip block includes the apex (block \( a \)) together with one additional atomic plane above. We considered several values for the surface-tip distance \( z \). The \( a \) and \( a \) matrix elements were obtained from a slab with a \( 2 \times 2 \) lateral periodicity containing the apex block \( a \), together with three Cu atomic planes.

Once all these fragments were calculated, we extracted the k-matrix elements we need. We then calculated all the lacking k points by symmetry according to Eq. (6), and we finally combined the different k-matrix elements using Eq. (7) to obtain the real-space matrix elements.

B. Influence of the accuracy of the DFT calculation

In our first calculation of the tunneling current, which we considered as a reference calculation, the different fragments depicted in Sec. IV A 2 were calculated with \( N_{\xi}^{\text{DFT}} = 16 \) for slabs with a \( 1 \times 1 \) periodicity as well as for slabs with a \( 2 \times 2 \) periodicity.

The relative accuracy of the integrals was set to \( 10^{-4} \), and the LDA potential was employed. In all the fragments, the AO’s of the Cu atoms were frozen up to \( 3p \), and the valence AO’s were described by the basis set 1 (see Table I), which corresponds to a double-\( \xi \) s and single-\( \xi \) p and d basis set. For all the fragments, we used a standard fit-functions set from the ADF-BAND package made of 13s, 7p, 6d, 3f and 2g Slater-type AO’s which will be denoted as fit1 in the following. The conductance \( \sigma \) was calculated for all \( z \) distances considered, using the same 16 bulk k points as in the DFT calculations (i.e., we defined a \( 4 \times 4 \) supercell for the entire STM system). From now on, \( N_{\xi} \) stands for this number of bulk k points used for the current calculation. The zero-bias limit was considered and, consequently, the electrons propagate at the bulk Fermi energy. This will be the case for all the calculations in this article.

The calculated conductance \( \sigma \) was divided by the number of apex in the supercell, e.g., 4 in the case of a \( 4 \times 4 \) supercell. The result is shown in Fig. 3. For large \( z \) distances, \( \log_{10}(\sigma) \) varies linearly with \( z \). The estimated slope \( [d \log_{10}(\sigma)/dz] \) (calculated between \( z = 7 \) and 8 Å) is \(-0.96\), in very good agreement with the experimental value \(-1\). Indeed, it is well known that the current decreases about one decade per Å. We should underline that this value was obtained by means of standard conditions in the ADF-BAND calculation and without fitting any parameters. At short tip-surface distances, a phenomenon of saturation is observed and the absolute slope value decreases. We investigated how much the levels of accuracy in our DFT calculations could influence the estimation of the tunneling current.

(1) Besides the reference basis set 1, we considered two additional ones, namely, basis set 2 and basis set 3. The

![FIG. 3. Calculated conductance \( \sigma \) as a function of the tip-surface distance for the bare Cu(001) probed by a Cu tip. Three basis sets were tested (see Table I). Results using the GGA and LDA exchange-correlation potentials are also shown. The slope value \( [\delta = d \log_{10}(\sigma)/dz] \) is indicated, determined for large tip-surface distances.]

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TABLE I. The character and the exponent of Slater functions for the valence basis sets of Cu and S atoms. NAO is a numerical atomic orbital obtained from a Herman-Skilmann-type calculation. The atomic orbitals (AO’s) up to 3p are frozen for Cu and for S, and AO’s up to 2p are frozen.
former corresponds to basis set 1 plus $d$ Slater orbitals, and the latter to basis set 2 plus Slater diffuse $p$ orbitals. All these basis sets are described in Table I. However, we limited the use of basis set 3 to junction atoms ($a$ and $r$ blocks), while $s$ and $t$ blocks were described by basis set 2. The net effect of basis set change can be seen in Fig. 3. The slope value is weakly affected and remains close to $-1$. Conversely, the conductance value is significantly increased when using a more diffuse basis set, e.g., basis set 3. This is the reflection of the strong interaction between the diffuse $p$ orbitals of the surface interact with the $p$ diffuse orbitals of the apex.

(2) The influence of GGA exchange-correlation potential was traced. The result is shown in Fig. 3. No significant modifications were observed either for the slope value or for the conductance.

(3) The role of the number of $k$ points used in the DFT calculation was tested by performing the same calculations on the fragments with $N_{k}^{DFT} = 64$ for $1 \times 1$ slabs only ($N_{k}^{DFT}$ remains equal to 16 for $2 \times 2$ slabs). We found that the current was affected by less than 13%, and that the slope was not changed compared to the reference calculation. We can conclude that the DFT-derived matrix elements are already well converged with the $k$ sampling used in our reference calculation.

(4) Several types of fit-functions sets were compared. A second standard fit-functions set, namely fit2, built on 15$s$, 7$p$, 6$d$, 4$f$, and 3$g$ Slater AO’s, was tested. As the error in the electronic density of the surface-apex slab was somewhat large with the standard fit-functions sets (fit1 and fit2), we designed an augmented fit-functions set fit3 which contains a larger number of more diffuse orbitals. Even though the electronic density between the surface and the apex is not properly described with fit1 and fit2, the value of the tunneling current is only affected by less than 1%.

(5) A $10^{-4}$ criterion for numerical integrations leads to a well-converged value of the conductance calculation.

C. Influence of the parameters used in the current calculation

1. Number of $k$ points

In Fig. 4(a), we present the $\log_{10}(\sigma)$ curves ($\sigma$ in $2e^2/h$) units as a function of the $z$ tip-surface distance in Å, for several bulk $k$ samplings ($N_k^1$= 4, 16, 64, and 256) used for the tunnel current calculation. The calculated conductance was normalized to one tip apex. The apex is on a hollow site and the model used to describe the tunnel junction is the same as before. Matrix elements for the fragments were calculated with $k$ samplings $N_{k}^{DFT}$=64 and $N_{k}^{DFT}$=16 for the $1 \times 1$ and $2 \times 2$ slabs, respectively. One should note that the $k$ sampling may be larger in the tunneling current evaluation than in the DFT calculations (see Sec. III B). Although the slope value $[d \log_{10}(\sigma)/dz]$ is hardly affected by the number of bulk $k$ points used in the current calculation, the conductance $\sigma$ is significantly modified.

In Fig. 4(b), we plot $\sigma$ as a function of $(N_k)^{1/2}$ for a tip-surface distance of 7 Å. For each $k$ sampling, $\sigma$ was normalized to one tip apex. For $N_k \geq 256$, the conductance varies by less than 10%. Therefore, the conductance can be considered to be converged for a $16 \times 16$ supercell.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{(a) Calculated conductance $\sigma$ as a function of the tip-surface distance for the bare Cu(001) surface probed by a Cu tip. The number of bulk $k$ points ($N_k$) was varied. The slope value \[\delta = d \log_{10}(\sigma)/dz\] is indicated. (b) $\sigma$ as a function of $(N_k)^{1/2}$ for a tip-surface distance of 7 Å.}
\end{figure}

2. Influence of the model

Within our approach, the model system is decomposed into PL’s in the direction perpendicular to the surface, and only the matrix elements between nearest-neighbor blocks are taken into account. The thicker the blocks, the more realistic this approximation. The influence of the number of layers for the description of the surface block $r$ was studied for a given tip-surface distance of 7 Å. In the reference calculation, $r$ was described by two atomic layers. Models with one, two, and three atomic planes were then considered. The fragments used in the DFT calculations remained unchanged (see Sec. IV A 2) except for the tip-surface fragment where the surface $r$ now contains three atomic planes. This tip-surface fragment was calculated at the same level of accuracy as for the reference calculation ($16 \times k$ points in the BZ of the $2 \times 2$ cell. $10^{-4}$ integrals evaluation accuracy, basis set 1, and fit-functions set fit3).

The calculated tunnel conductance $\sigma$ as a function of the number of layers in the surface block $r$ is given in Table II. 16 bulk $k$ points were used, and the conductance was normalized to one tip apex. The limitation to a single layer is clearly not correct since it yields a tunnel conductance almost twice as large as the one for thicker block models. The inclusion of the surface second layer in the calculation decreases the tunnel current. Besides the difference in the model itself, some destructive interference effects are partly responsible for the decrease of the current. This can be seen

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Model & One layer & Two layers & Three layers \\
\hline
$\sigma$ & $1.01e^{-3}$ & $5.34e^{-4}$ & $5.54e^{-4}$ \\
\hline
\end{tabular}
\caption{The conductance $\sigma$ as a function of the model chosen for the surface block $r$. One, two, and three layers were considered for $r$. The tip apex is on a hollow site and the tip-surface distance was set to 7 Å.}
\end{table}
by inspecting the decomposition of the conductance in contributions of the apex and surface orbitals given in Table III. The main contribution to the transmission coefficient comes from the interaction between the 4s orbital of the Cu atom at the extremity of the apex (Cu a) and the 4s orbitals of the Cu atoms at the first surface layer (Cu 1). It contributes up to 50% to the total transmission coefficient. The 4s AO’s of the four Cu apex atoms above Cu a (Cu a2) also strongly interact with the 4s AO’s of Cu 1, since they contribute up to 36% to the total transmission coefficient. Due to destructive interferences between the 4s AO’s of Cu 1 and the 4s AO’s of the surface second-layer Cu atoms (Cu 2), the contribution arising from the interaction between the latter and the 4s AO’s of Cu a decreases the total transmission coefficient by ~10.5%. By summing the transmission coefficients over all the tip apex AO’s, the contribution of the first surface layer (124%) is decreased by the atoms of the second layer by ~28%. Consequently, the surface block must at least be described by two atomic layers. The third layer in the surface has a negligible influence in the tunnel current, so that the reference calculation with two atomic planes can be considered as a fair approximation.

D. Position of the tip and nature of the tip apex

We studied the conductance when the tip apex is on top of a surface Cu atom. The model we adopted is identical to the one described in Sec. IV A 1. We used the same matrix elements as in Sec. IV C 1 except for the matrix elements between r and a, for which we performed calculations moving the tip apex on top of a surface Cu atom. The DFT parameters used for this calculation are the same as for the reference calculation, except for the 1×1 periodic slabs where \( N_k^{DFT} \) was set to 64. 64 bulk \( k \) points were used for the current calculation. We found that the conductance is slightly larger for the top position than for the hollow one for all the selected tip-surface distances (from 3 to 8 Å). The obtained corrugation is significant only for small resistances, about 0.02 Å for 100 kΩ. The corrugation is neither significantly sensitive to any applied finite bias nor the use of basis set 3.

It was experimentally shown that the corrugation is indeed very small for Cu(001) probed by a metallic tip.23 We replaced the Cu tip apex by a S tip apex. The distance between S and the Cu plane of the apex was set to 1.25 Å. We used the same fragments as in the previous study, but the \( a \) block is made of a S atom at its extremity. The basis set for the S atom is described in Table I. We adopted the same model as in Fig. 2. The conductance was evaluated with 64 bulk \( k \) points, and normalized to one tip apex. In comparison with the Cu tip, the resulting conductance curve is shown in Fig. 5(a) for the hollow position. For tip-sample distances \( z > 4 \) Å, we found that the conductance for the S tip is smaller than for the Cu tip by a factor ~2.5. The absolute slope

![Image](image_url)

**TABLE III.** Main individual components \( T_{ja}(r_j,a_j)(\times 10^{-5}) \) of the total transmission coefficient \( T \) for the bare Cu(001) surface probed by a Cu tip. The rows in the table refer to the \( r \) surface AO’s, while the columns correspond to the apex \( a_j \) AO’s. Cu a represents the atom at the extremity of the apex. Cu a2 corresponds to the four Cu atoms of the apex above Cu a. Cu 1 (Cu 2) represents the four atoms of the first (second) layer of the surface. Tip-tot (surface-tot) corresponds to the summation of the transmission coefficients over all the tip apex AO’s (surface AO’s). Only the components that contribute in absolute value by more than 1% to \( T \) are indicated in the table. The tip-surface distance was set to 7 Å.

<table>
<thead>
<tr>
<th>Orbitals</th>
<th>Cu a 2-s</th>
<th>Cu a-( d_{z}^{2} )</th>
<th>Cu a-( s )</th>
<th>Cu a-( p_{z} )</th>
<th>Tip-tot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 1-s</td>
<td>21.26</td>
<td>6.85</td>
<td>29.52</td>
<td>5.67</td>
<td>64.01</td>
</tr>
<tr>
<td></td>
<td>(36.0%)</td>
<td>(11.6%)</td>
<td>(50.0%)</td>
<td>(9.6%)</td>
<td>(108.4%)</td>
</tr>
<tr>
<td>Cu 1-p_{z}</td>
<td>1.89</td>
<td>2.36</td>
<td>5.9</td>
<td>9.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(3.2%)</td>
<td>(4.0%)</td>
<td>(10.0%)</td>
<td>(16.0%)</td>
<td></td>
</tr>
<tr>
<td>Cu 2-s</td>
<td>-6.85</td>
<td>-2.18</td>
<td>-6.20</td>
<td>-1.00</td>
<td>-16.53</td>
</tr>
<tr>
<td></td>
<td>(-11.6%)</td>
<td>(-3.7%)</td>
<td>(-10.5%)</td>
<td>(-1.7%)</td>
<td>(-28.0%)</td>
</tr>
<tr>
<td>Surface-tot</td>
<td>15.35</td>
<td>5.73</td>
<td>30.65</td>
<td>5.02</td>
<td>59.05</td>
</tr>
<tr>
<td></td>
<td>(26.0%)</td>
<td>(9.7%)</td>
<td>(51.9%)</td>
<td>(8.5%)</td>
<td>(100%)</td>
</tr>
</tbody>
</table>

**FIG. 5.** (a) Calculated conductance \( \sigma \) as a function of the tip-surface distance for the bare Cu(001) surface probed by two different tips: tip Cu (S) corresponds to a Cu tip with a Cu (S) atom at the extremity of the apex. The number of bulk \( k \) points was set to 64. The slope value \( [\delta = d \log(\sigma)/dz] \) is indicated for the two tips, determined for large tip-surface distances. The two tips are above a hollow site. (b) Calculated image corrugations as a function of the gap resistance for the two different tips [same conditions as in (a)].
value for \( \log_{10}(\sigma) \) versus \( z \) is slightly larger for the S tip, which corresponds to an increased tunnel barrier, and arises as a consequence of a smaller spatial extent of the S atomic orbitals.

The corrugation as a function of the resistance is shown in Fig. 5(b) for both the Cu and S tip apexes. The corrugation is still small for the S apex but larger for the Cu apex. For a 1-M\( \Omega \) gap resistance, the calculated corrugation is about 0.005 Å. Experimentally, it was found that the atomic resolution image exhibits a 0.009 Å corrugation for the same value of the resistance but with an acetylene tip.\(^3\) It is experimentally well known that the corrugation varies between a metallic and a nonmetallic atom at the apex. A nonmetallic tip apex generally provides a larger corrugation.\(^2\)

V. Cu(001) + \( p(2 \times 2) \)-S PROBED BY A CU TIP APEX

A. Model and fragments adopted

The tunnel current was calculated for a \( p(2 \times 2) \) overlayer of S atoms on the Cu(001) surface. The model we adopted is very similar to the one described in Fig. 2. The blocks \( a, s, \) and \( t \) are identical to the ones of Fig. 2. The surface block \( r \) consists of a layer of Cu atoms and one S atom adsorbed at the fourfold hollow site, resulting in a \( 2 \times 2 \) superlattice. The distance between S and the atomic plane below is set to 1.25 Å. Since the apex and the two bulks are not modified with respect to the clean Cu(001), their corresponding Hamiltonian and overlap matrix elements \((aa, at_1, t_1t_1, s_1s_1, l_1l_1)\) may readily be used for the current system. In order to obtain the matrix elements for \( rs_1 \) and \( rr \), we performed a DFT calculation on a fragment with a \( 2 \times 2 \) periodicity containing four Cu layers with one S atom adsorbed on top in a fourfold hollow position. This calculation was done with 16 \( k \) points in the BZ, a \( 10^{-4} \) accuracy for the integrals evaluation, the fit-functions set fit1, the basis set 1 for the Cu atoms and basis set 4 for the S atom (see Table I). As for the matrix elements between \( a \) and \( r \), we considered a \( 2 \times 2 \) slab where the surface \( r \) is modeled by two Cu layers with one S atom on top, while the tip consists of two Cu layers with one Cu atom adsorbed below. In this case, we define the surface-tip distance \( z \) as the difference between the Z coordinates of the Cu apex atom and the S adsorbate. One should note that the \( z \) origin adopted here is different by 1.25 Å from the one for the bare Cu(001) surface. We performed several calculations for different \( z \) values and two apex positions: on top of the S atom (top position) and at the center of the square formed by four S atoms (hollow position).

B. Results

The conductance \( \sigma \) was calculated as a function of the \( z \) distance for the top and hollow positions. We considered the zero bias limit and used 256 bulk \( k \) points, i.e., the supercell is \( 16 \times 16 \times 16 \). The conductance was normalized to one tip apex. The results are shown in Fig. 6(a). The top position provides a current larger than the hollow position by a factor of 1.7 for the same tip-surface distance. For \( z > 4 \) Å, the two curves display a linear behavior and the slopes are \(-0.97\) and \(-1.02\) for the hollow position and the top position, respectively. The difference in the slopes suggests that an image in the \( d \log_{10}(\sigma)/dz \) mode ("work-function" imaging) could be possible in that case.

A current analysis was performed to understand why the current is larger when the tip apex is on top of a S atom. The contributions of the surface AO’s to the transmission coefficient are listed in Table IV. We summed the transmission coefficients \( T_{ra}(r_i, a_j) \) over all the AO’s \( a_j \) of the tip apex [see Eq. (5)], and the result is given for each surface AO \( r_i \) and for the two tip positions. The difference \( \Delta[I_{T_{ra}^{top}}(r_i) - I_{T_{ra}^{hollow}}(r_i)] \) is also indicated. The main AO contribution for the apex is the 4s orbital of the Cu apex atom. The analysis of the current was done for a given tip-surface distance of 7 Å and for 64 bulk \( k \) points.

The contributions of the surface atoms to the tunnel current are clearly different for the two tip positions. For the top position, S 3p\(_z\) gives the largest current value but the S 3s orbital shows destructive interference effects and negatively contributes to the current. As a result, the total contribution of the S atom to the transmission coefficient is reduced to 18%, and the contribution of the four Cu surface atoms is dominant (79%, mainly from the 4s orbitals, the other AO’s contributing by less than 2%). For the hollow position, when the tip is between the S atoms, the contribution of all the surface AO’s is reduced. The participation of the S 3p\(_z\) orbital shows destructive interference effects and negatively contributes to the current. As a result, the total contribution of the S atom to the transmission coefficient is reduced to 18%, and the contribution of the four Cu surface atoms is dominant (79%, mainly from the 4s orbitals, the other AO’s contributing by less than 2%). For the hollow position, when the tip is between the S atoms, the contribution of all the surface AO’s is reduced. Therefore, the S contribution is reduced by a factor of 7 compared to the top tip position, and the contribution of the four Cu surface atoms largely dominates the current. It is important here to underline that although the S atom is positioned at a higher Z coordinate than the surface Cu atoms,
the calculation indicates that for both tip positions, the main part of the tunnel current arises from the surface Cu atoms. The S 3p_z AO mostly contributes to the contrast between the top and hollow positions (133%). The S 3s AO also greatly affects this current difference, but due to destructive interferences it decreases the value of the contrast by ~93%. Unlike previous studies on related systems which employed a semiempirical Hamiltonian,\textsuperscript{22,24} this AO plays a major role. Due to the destructive interferences from the S 3s AO, the contribution of the S atom to the contrast is reduced to 36%, whereas the Cu atoms contribute up to 58%. The interaction with the S atoms alters the Cu surface electronic properties and the tunnel current through the Cu atoms becomes strongly corrugated.

In order to characterize the influence of the interferences in the image contrast, we performed a calculation of the tunnel current without any interferences. This means that we considered the contribution of an electron tunneling from the surface AO \( r_1 \) to the tip apex orbital \( a_j \) in the absence of interference with any other tunneling paths.\textsuperscript{12} The tunnel current is increased by a factor of ~4 for each tip position, a clear indication of the strong influence of destructive interference effects. These latters affect all the surface AO’s contributions but to different degrees. They decrease the tunnel current on the S atom by at least a factor of 10, whereas the participation of the surface Cu atoms is only reduced by a factor of 3. The S atom contributes up to 61% and the Cu atoms up to 32% to the current modulation. This confirms that the small contribution of the S atoms in the image contrast results from the destructive interferences. When the tip-surface distance decreases, the main conclusions on the origin of the contrast remain the same.

We also studied the corrugation as a function of the gap resistance for several bulk \( \mathbf{k} \) samplings. The results are shown in Fig. 6(b). As expected, a decrease in the corrugation as the tip is withdrawn from the surface was always found while the gap resistance increased. For a bulk \( \mathbf{k} \) sampling \( N_k \geq 256 \), the corrugation is affected by less than 5%, and can already be considered as well converged. A similar convergence criterion was also found for a related system based on a H\"{u}ckel-type Hamiltonian.\textsuperscript{22} For a resistance equal to 10 \( \text{M} \Omega \) and \( N_k = 256 \), we found that the corrugation is about 0.25 Å, which is in good agreement with the experimental value obtained by Gauthier.\textsuperscript{25}

In order to obtain a better understanding of this \( \sigma \) vs \( \mathbf{k} \) behavior, dispersion curves for the transmission coefficient are plotted in Fig. 7 for the bare Cu(001) surface and the Cu(001) + \( p(2 \times 2) \)-S one. These curves look very much like the usual band diagrams. As a striking feature, they exhibit two dips between \( \Gamma \) and \( X \) and \( M \) and \( \Gamma \). We traced the origin of these depressions observed for both surfaces in two ways. The current value without interferences was calculated and is reported in Figs. 7(a) and 7(b) (dashed lines). Dips are still present, but their amplitude is significantly reduced. Therefore, they are associated with areas of strong destructive interferences. Conversely, far from these dips, the participation of these interferences is smaller. One can explain this obser-

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>S</th>
<th>S s</th>
<th>S ( p_z )</th>
<th>S ((p_x + p_y))</th>
<th>4 Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>8.17</td>
<td>1.45</td>
<td>-5.54</td>
<td>7.36</td>
<td>-0.37</td>
<td>6.44</td>
</tr>
<tr>
<td></td>
<td>(100%)</td>
<td>(17.7%)</td>
<td>(-67.8%)</td>
<td>(90.1%)</td>
<td>(-4.6%)</td>
<td>(78.8%)</td>
</tr>
<tr>
<td>Hollow</td>
<td>3.62</td>
<td>-0.21</td>
<td>-1.29</td>
<td>1.29</td>
<td>-0.2</td>
<td>3.79</td>
</tr>
<tr>
<td></td>
<td>(100%)</td>
<td>(-5.7%)</td>
<td>(-35.7%)</td>
<td>(35.7%)</td>
<td>(-5.6%)</td>
<td>(104.8%)</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>4.55</td>
<td>1.652</td>
<td>-4.25</td>
<td>6.07</td>
<td>-0.17</td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>(100%)</td>
<td>(36.3%)</td>
<td>(-93.0%)</td>
<td>(133.4%)</td>
<td>(-3.7%)</td>
<td>(58.2%)</td>
</tr>
</tbody>
</table>

![Fig. 7](image-url)
vation by looking at the reduced number of bulk propagative channels in these locations of the BZ, as shown in Fig. 7(c). Therefore, the dips can be seen as resulting from two effects: a small number of channels, and on the other hand a modulation of destructive interferences with respect to the k point. The presence of the dips in the BZ and the associated fast variation of the conductance demand a rather dense array of k points to obtain a converged value of the total conductance. For the bare Cu(001) surface [Fig. 7(a)], the current peaks in the neighborhood of Γ with a rather fast decay when going to the BZ edge. This is consistent with a simple STM junctions model, where electrons with |k| = 0 correspond to larger currents. The dispersion curves of the transmission coefficients for the p(2×2)S on Cu(001) surface are much more complicated due to a stronger corrugation of the wave function [see Fig. 7(b)]. The maximum current is no longer observed near Γ but close to the zone boundaries, particularly for the top position. This means that the channels with a nonzero k∥ play a major role in the tunneling process. A calculation limited to Γ, corresponding to a minimal 2×2 supercell, would give a larger current between S atoms and a reversed contrast. Therefore, for a correct description of image corrugation, a good balance between the k points samplings around the BZ center and its edges must be achieved and requires a rather dense array of k points.

VI. CONCLUSIONS

Our method for STM image calculations combines a multiple-scattering formalism for the evaluation of the tunnel current and a first-principles DFT determination of the electronic structure. It should be emphasized that the atomic structures of both the sample and tip are realistically described. The coupling of the surface and tip apexes to their respective bulk reservoirs and the interaction of the tip apex with the surface are fully taken into account. First, the matrix elements of the Hamiltonian were self-consistently determined from DFT calculations on slabs modeling all fragments in the STM system. They were then used to evaluate the tunneling current with a Green’s-function technique. We applied our method to the Cu(001) and Cu(001) + p(2×2)-S surfaces. The conductance σ in zero bias limit was evaluated as a function of the tip-surface distance z and the corrugations were deducted. The slope value [d log10(σ)/dz] is close to −1 for all the selected examples. The calculated corrugation for the bare Cu(001) surface is small and only measurable at small gap resistances. A S atom at the tip apex enhances the corrugation. For the Cu(001) + p(2×2)-S surface a rather large corrugation of 0.25 Å is found. All these results agree with experimental observations. The influence of different approximations both in the DFT and the tunneling current calculations were investigated. It is shown that the choice of the AO basis set does not affect the slope value [d log10(σ)/dz], but the current value can be significantly increased when using very diffuse AO’s in the basis set. The number of bulk k points used in the calculation of the current must be large enough to obtain a satisfactory convergence in the conductance value and the corrugation. The analysis of the atomic orbital contributions to the tunnel current provides insights into the STM contrast mechanism. For the Cu(001) + p(2×2)-S system, the main part of the tunnel current arises from the surface Cu atoms, although the S atom is at a higher Z value. This partly results from a strong destructive interference effect of the S 3s orbital. With similar arguments, we also proved that the image corrugation for the p(2×2)S on Cu(001) surface is due mainly to a modulation of the current coming from the surface Cu atoms and, to a smaller extent, to the contribution of S atoms. The small contribution of S atoms results from the destructive interferences of the S 3s AO.

Although the applications presented here were performed in the zero-bias limit, the method enables to apply a finite voltage between the tip and the sample. Such scanning tunneling spectroscopy simulations are now under investigations.

ACKNOWLEDGMENTS

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*ab initio* calculation, rendering the corresponding calculation untractable. However, the Cu atom at the extremity of the apex is separated by 5 Å from its periodic image, so that lateral interactions should be weak. An extended Hückel test calculation has shown a small change (~10%) in the tunneling current between a periodically repeated and an isolated tip model for a 7-Å tip-sample distance. Work along this line is in progress via the use of alternative *ab initio* formalisms.

25 S. Gauthier (private communication).