

Simulation of STM Images from Commercially Available Software

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Abstract: The simulation of scanning tunneling microscopy images is performed ab initio with two readily available programs (Gaussian94 and a commercial spreadsheet). The model requires only a series of matrix multiplications and lends itself to widespread use. The versatility, reliability, and wealth of data one can obtain from the approach are illustrated by three examples: (i) benzene adsorbed onto the Rh(111) surface, (ii) naphthalene on the Pt(111) surface, and (iii) *trans*-2-butene on the Si(100) surface.

Introduction

Chemists and physicists alike have been exploring size domains that range from the macroscopic to the microscopic in the attempt to bend, tune, and ultimately control the properties of matter for their needs and desires. Information retrieval from single molecules and the ability to manipulate them individually is one of the fundamental steps toward this objective. Probing scanning microscopies, in general, and scanning tunneling microscopy, in particular, are elegantly suited to achieve the molecular resolution level.¹ Single molecules are also routinely explored by quantum molecular theory, a routine that has not yet been entirely extended to the simulation of STM images. In refs 2–5 a recent comprehensive review and other important references for the ab initio simulation of images are, however, given. The models^{2–5} cannot be considered of widespread use, especially among the experimentalists, and we felt that there is a demand to present a relatively simple approach, able to assist and complement the very experiments that can bestow information on one molecule at a time. Whereas, to the best of our knowledge, no custom-ready computer package exists to generate ab initio scanning tunneling microscopy, STM, images, we intend to show that it is nonetheless possible to obtain them with a little effort with the use of two commercially available programs (a quantum chemical program and a commercial spreadsheet). Rather than dwelling on the model which is briefly presented below, we illustrate the procedure in rather general terms using three examples. The first is the case of benzene adsorbed onto the Rh(111) surface, the second is naphthalene on the Pt(111) surface, and the third is *trans*-2-butene on the Si(100) surface. Benzene and naphthalene were selected to represent the important class of aromatic systems. Their conjugated π -electron framework provides them with low-lying unoccupied molecular orbitals that are readily accessible in an STM experiment. Importantly, the nontrivial nature of their images becomes evident if one considers that their symmetry

is lower than that of the isolated molecule. Chemisorbed *trans*-2-butene was chosen because it represents one of the most recent success stories of scanning tunneling microscopy which was shown to be able to differentiate between two enantiomers of the same molecule. The removal of the π -electrons in the chemisorption and the nonplanarity of the system add further complexity—with respect to the previous two examples—in the simulations.

Computational Background

Molecular orbital energies and wave functions along with related quantities (overlap integrals) were obtained ab initio with the widely available Gaussian94 program,⁶ while the individual "pixels" that form the simulated image were obtained in two steps which entailed (i) a series of matrix multiplications, and (ii) weighing of the matrix elements by a factor which is a function of the energy difference between the unperturbed levels. The constant current of the experiments was then obtained, only for nonplanar systems (see below), by three-point interpolation of the data obtained at different distances between tip and sample. Representation of the images was produced with a commercial spreadsheet. Importantly, in the present approach, tip, sample, and substrate are considered explicitly in a cluster-type approach.

More in detail, the matrix element for transfer of an electron from the i -th to the j -th orbital, H_{ij} , is contained in the interaction matrix, $H = C_0^\dagger S_1 C_1 \epsilon_1 C_1^\dagger S_1 C_0$, formed by the molecular orbitals, C_0 , calculated with tip and substrate at infinite distance, indicated by the subscript 0, while the molecular orbitals, C_1 , their eigenvalues, ϵ_1 , and the overlap matrix between the atomic orbitals, S_1 , were obtained by the first self-consistent field iteration of interacting tip and substrate, using the C_0 orbitals as a guess. When 0 and 1 coincide, the approach yields the molecular orbitals energies. When they differ, as is the case in practice, it is equivalent to that given in ref 3 where the relevant equations are expressed in terms of integrals over molecular orbitals.

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To account for the non perfect degeneracy of the two orbitals involved in the transfer, we use the result of time-dependent perturbation theory applied to two interacting levels i and j which allows us to write the rate constant of a transfer process as

$$k \propto \frac{2}{a(\eta) + 2}$$

where

$$a(\eta) = tg^2\eta + \frac{1}{tg^2\eta}$$

and the relation

$$tg2\eta = \frac{2H_{ij}}{H_{jj} - H_{ii}}$$

holds. The proportionality in the description of the rate constant, k , arises from the presence of two distinct consecutive processes. The first is the transport of an electron or a hole from tip to sample, the second from sample to the bulk. More in detail, the perturbation mixes the localized initial state, Ψ_0 , with the charge transfer state, Ψ_{i-j} , where the particle has gone from the tip to the sample. The time evolution of this system is described as

$$|\langle \Psi(t) | \Psi_{i-j} \rangle|^2 = \frac{2}{a(\eta) + 2} \left[1 - \cos\left(\frac{2\pi(\epsilon_j - \epsilon_i)}{h} t\right) \right]$$

The state is then neutralized by the bulk with a rate constant k_n that does not depend on H_{ij} and that occurs on a time scale slower than the tip-to-sample transfer. In practice

$$k = k_n [2/(a(\eta) + 2)]$$

so that the current, I , is given by $I = ke$. The applied potential, V , can reduce the energy difference between the local states of tip and sample by $e|V|$. Although, in principle, one could decrease the energy gap by this amount, in the present case, the large $H_{jj} - H_{ii}$ difference would hardly be affected.

Finally, since most measurements are obtained at constant current, while the calculations are naturally performed at constant height, it was necessary to go from one regime to the other. Since the current decreases nearly exponentially with the sample-tip distance, z , one can assume that it follows an equation of the type $\log I = \log I_0 + az + bz^2$ and calculation of the transfer probability at three points can be used for the interpolation. Importantly, the unknown constant k_n is not required to understand the contrast mechanism in the STM experiment because it is effectively canceled out in the step calculating the constant current image.

Results

The versatility and accuracy of the present model can be appreciated by examining the images of Figure 1. The first is benzene adsorbed onto the Rh(111) surface,⁷ the second is naphthalene on the Pt(111) surface,⁸ and the third is *trans*-2-butene adsorbed on the Si(100) surface.⁹ The three examples

were chosen because of the nontrivial nature of their images and also because no previous ab initio simulation had been performed before at this level with the explicit inclusion of the metallic/semiconducting substrate.

Benzene on Rh(111). This was the first ever STM image obtained at molecular resolution.⁷ In reality, benzene is coadsorbed with CO in a $(3 \times 3)(\text{C}_6\text{H}_6 + 2\text{CO})$ ordered structure. The STM image (see for comparison Figures 3 and 4 of ref 7) shows three minima and three maxima and therefore forfeits the 6-fold symmetry of the isolated molecule. The minima appear when the CC bond is positioned on the top of a Rh atom, while the maxima are localized on the remaining CC bonds. A well-defined minimum is present at the center of the ring. Previous semiempirical simulations showed that the 3-fold symmetry is not due to molecular deformations.¹⁰ The geometry of a cluster of six atoms of Rh with one molecule of benzene was taken from ref 11. The basis set of atomic orbitals was D95¹² while the Rh atoms were treated with the LANL2DZ pseudopotential.¹³ The tip was represented by a single tungsten atom. Negative charge flow went from tip to sample. The simulation was performed at constant (3.5 Å) height since for planar systems we found that there is hardly any difference between constant current and constant height. The tip-substrate distance is intermediate between those used in refs 3 and 4. Discussion of the variation of the theoretical simulation as a function of tip-substrate separation can be found in ref 2. Figure 1a shows the simulated image characterized by the three maxima on the CC bonds and the central minimum. It also illustrates the fundamental role played by the adsorbing substrate without which it would be impossible for the calculations to privilege the Kekule structure whose double bonds lie above Rh atoms.

In agreement with the semiempirical results, the 3-fold symmetry of the image arises because of the variation of the electron-transfer probability induced by the metallic surface.

Naphthalene on the Pt(111). The STM images of naphthalene can be found in ref 8, in particular, Figure 1a of that work which allows explicit observation of the double ring structure of the molecule. The images do not show simultaneously naphthalene and the surface so that a hypothesis must be made about the nature of the adsorbing site.^{14,15} The geometry of a cluster of 11 Pt atoms with 1 molecule of naphthalene was taken from ref 14. The basis set was D95¹² while the Pt atoms were treated with the LANL2DZ pseudopotential.¹³ The tip was represented by a single Pd atom. The current flow went from tip to sample. The simulation was performed at constant (3.8 Å) height.

Figures 1b and 1c show the simulated image of the isolated and adsorbed molecules. In the simulation, upon adsorption, one can notice the shift of the maximum from the central part of the molecule to the edges in nice agreement with the experiment whose naphthalene images were described as bilobed.⁸ This emphasizes once again the role played by the substrate in STM images, *a role that the cluster model can capture.*

***trans*-2-Butene on Si(100).** This system has been studied very recently to prove that STM images can assign the absolute configuration of adsorbed enantiomers.⁹ Silicon and hydrogen

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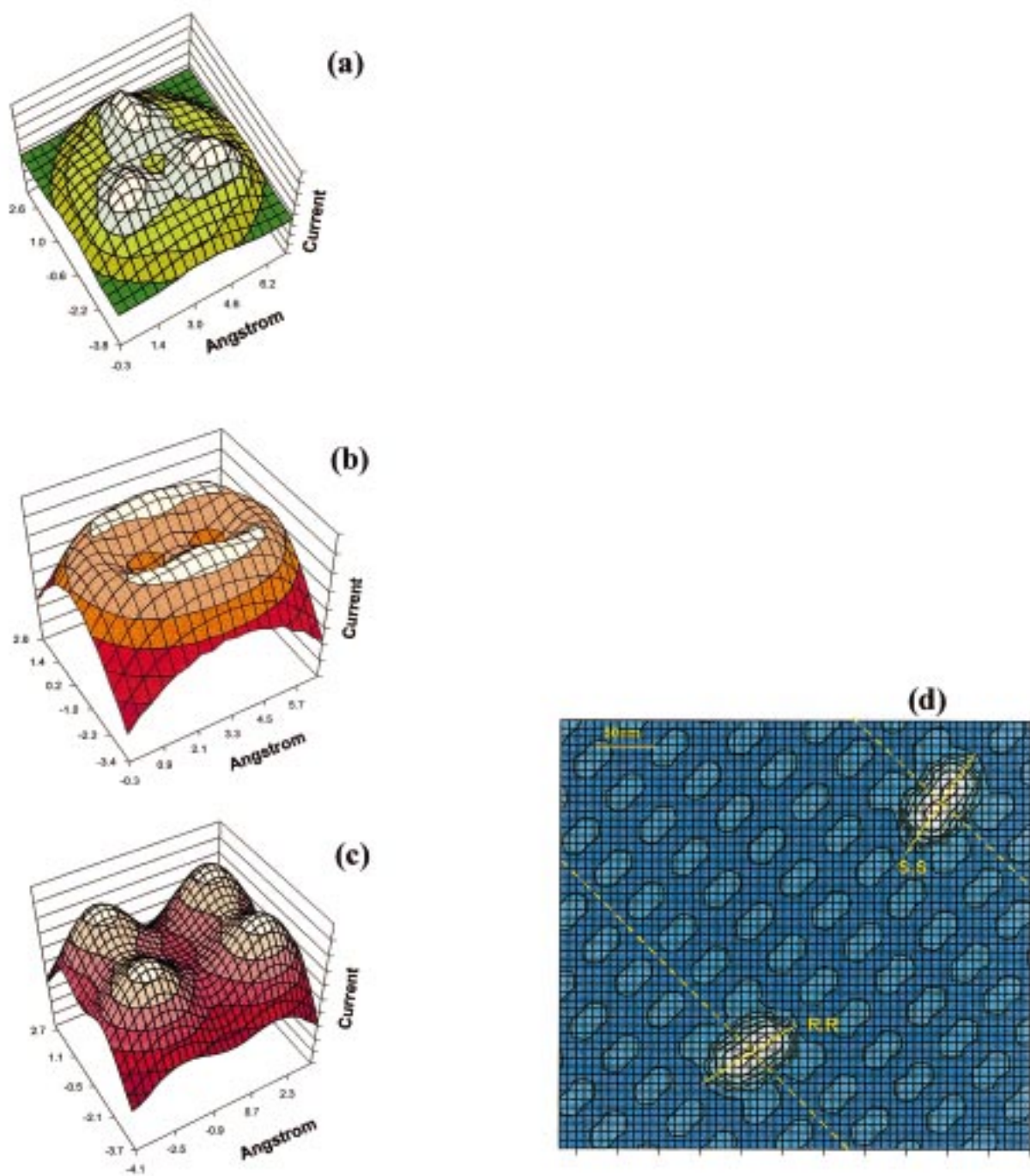


Figure 1. *Ab initio* simulated images of (a) benzene chemisorbed onto the Rh(111) surface (see for comparison figures 3 and 4 of ref 7), (b) isolated naphthalene, (c) naphthalene on the Pt(111) surface (see for comparison Figure 1a of ref 8), (d) *trans*-2-butene on the Si(100) surface (see for comparison Figure 1b of ref 9). The colors are arbitrary and are only used to assist the eye.

atoms were treated at 6-31G level¹⁶ while polarization orbitals were added for carbons.¹⁷ The tip was a single Pd atom. The electron flow was from tip to sample. The images are obtained at constant current. In the analysis of the experiment the Si surface plays a major role.⁹ The simulation therefore commences with the image of the Si(100) surface and goes on to that of *trans*-2-butene bound to the Si atoms. The simulation used a Si cluster in which the dimer formed by the reconstruction lies on the top of eight atoms whose dangling bonds are saturated by hydrogens, Si₁₀H₁₂. The coordinates were taken from a diffrac-

tometric study.¹⁸ Figure 1d contains the image of the Si(100) surface—obtained as a repetition of that of the minimal cluster Si₁₀H₁₂—onto which the images of the SS and RR *trans*-2-butene + Si₂H₄ have been grafted. Experimentally, the identification of the absolute configuration used the angle formed between the line joining the two prominent lobes of *trans*-2-butene and the “Silicon valley” underneath. While the experimental angle is ~30° against ~15° of the simulation, identification of the absolute configuration by the model cannot be doubted (it would be if the angle were close to 0° so that the two mirror images would coincide). It may be expected that in more complicated

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cases in which the enantiomeric nature of the chemisorbed molecules is not entirely evident from the experimental image, the present approach may be very useful.

Discussion and Conclusions

The ab initio simulation of STM images was performed at ab initio level through a procedure that requires only a series of simple steps. First the molecular orbitals of the tip and the substrate, i.e., molecule plus surface, are calculated separately. Then the interaction is switched on and a new set of molecular orbitals is generated—by the first iteration of the self-consistent field procedure—by bringing tip and substrate at “working distance” to give one of the pixels of the image. Noninteracting and interacting orbitals are used along with the overlap matrix and the eigenvalues to calculate the matrix elements of electron transfer by a straightforward series of matrix multiplications. The role of the nonperfect degeneracy of the initial and final orbitals in the transfer is accounted for by the analytical formula obtained by the time-dependent perturbation theory of two noninteracting levels. Also rather simply, when needed, the constant height calculations are turned into constant current ones

by 3-point interpolation. Since the most complicated step of the entire process is matrix multiplication, the use of the present model may lend itself to become of widespread use in the interpretation of the images.

The reliability of the model is assessed by examining the cases of benzene adsorbed onto the Rh(111) surface, naphthalene on the Pt(111) surface, and *trans*-2-butene on the Si(100) surface. The model reproduces the role of the metallic substrate which in the case of benzene reduces the 6-fold symmetry to 3-fold and in the case of naphthalene shifts the highest electron-transfer probability from the molecular center to its edges. It also captures the chiral nature of the STM image of the two enantiomers of *trans*-2-butene chemisorbed on the Si(100) surface. A similar accuracy may be expected in other forthcoming applications.

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