

**Contrast changes in STM images and relations between different tunneling models**

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A change in bias voltage can reverse the contrast of a scanning-tunneling microscopy (STM) image of an adsorbate molecule on a solid surface. This contrast change may take place not only in a case of tunneling in the neighborhood of a resonance level of the adsorbate, but it can also be seen in the case of a wide energy gap between highest occupied molecular-orbital and lowest unoccupied molecular-orbital levels. In order to find a unified description of contrast changes in STM images, we make comparisons between different approaches to tunneling. We especially consider the role of phase differences between possible tunneling channels. These phase differences can be related to the imaginary and real parts of the Green's function of the system which reveal whether the tunneling takes place through a resonant state or a forbidden gap. Finally, we compare experimental and calculated images of oxygen molecules on a silver surface and analyze the mechanisms of the contrast change in terms of phase shifts in different tunneling channels.

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**I. INTRODUCTION**

Scanning-tunneling microscopy (STM) produces images which reflect the local electronic structure rather than a real-space configuration of atoms on a solid surface.<sup>1</sup> A standard way to interpret STM measurements is to map the differential conductance onto the local density of states (LDOS) of the sample. This mapping can straightforwardly be derived from the Tersoff-Hamann approach to calculate tunneling currents.<sup>2</sup> However, a more exact elaboration of tunneling formulas reveals that the conductance of molecular adsorbates on the sample surface deviates from this approximation.<sup>3,4</sup> These kind of methods beyond the Tersoff-Hamann approach are, in general, based on Green's-function techniques. Although they seem to make the relation between the LDOS and STM image somewhat intractable, they enable one to analyze the contribution from different tunneling channels and their phase relations. Furthermore, these techniques applied to the adsorbate or impurity effects can be generalized to, e.g., magnetic impurities, as has been done in two recent studies.<sup>5,6</sup>

The complexity of the behavior of the tunneling current is especially seen in varying the bias voltage between STM tip and molecular samples on metal surfaces. There are two interesting points to note. First, certain molecules can be seen as relatively bright images although the tunneling takes place through a gap in the electronic structure of the molecule. Second, there are contrast changes within a rather narrow bias voltage variation for certain adsorbates. The first observation indicates that tunneling through a molecule is not completely inhibited even for a molecule with an energy gap at the Fermi energy. The second observation indicates that a considerable local change in tunneling current may take place within a small voltage range. On the other hand, the differential conductance is defined as the rate of change of current with respect to voltage,  $\sigma = dI/dV$ . According to the Tersoff-Hamann approach to tunneling, this change can be

attributed to a large LDOS of the sample. This approach predicts a direct proportionality between the local differential conductance and the LDOS of the sample:  $\sigma \propto \rho_s(\mathbf{r}, E)$ , where the energy and the bias voltage correspond to each other.<sup>2</sup> This approximation indicates that a contrast change could be observed merely when varying the bias voltage from one side of a resonant state of the adsorbate to the other. However, there are cases where the contrast change takes place in a gap between eigenstates of a molecular sample, which means that a large change in current cannot necessarily be related to a high LDOS.

Water on silver is an example of this kind of behavior.<sup>7</sup> The water molecule has a wide gap between highest occupied molecular-orbital (HOMO) and lowest unoccupied molecular-orbital (LUMO) states. Despite this, H<sub>2</sub>O on Ag(111) can be imaged as bright protrusions for some bias voltages corresponding to energies in the gap. In addition, there are rather sharp contrast changes for some bias voltages.<sup>7</sup> A rather sudden contrast change is also seen for oxygen molecules on silver as shown below. This change may be attributed to a high LDOS, but a more unified explanation for both of these examples can be found by considering the phase differences between different tunneling channels and the Green's function of the adsorbate.

A systematic study of the contribution of different routes to the tunneling current has been done by Sautet.<sup>8</sup> Using an extended Hückel model and linear chains with a direct "through-space" (TS) coupling and an indirect "through-adsorbate" (TA) coupling, a qualitative description for the images of a few adsorbate atoms on a metal surface can be found. First, in case of chemisorption, the adsorbate shifts and modifies the LDOS of the substrate, thus decreasing the tunneling current at the adsorption site. Second, an adsorbate always increases the probability of tunneling, but there is either constructive or destructive interference between TS and TA tunneling waves, which either increases or decreases the total current, respectively. That study presents a very

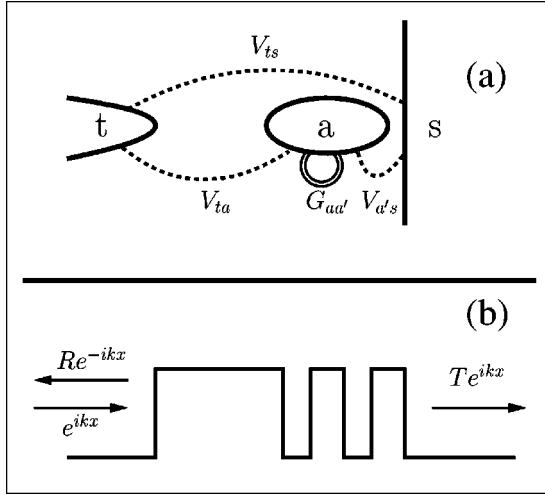


FIG. 1. The tunneling models used in this article. (a) A schematic construction of the tip-adsorbate-substrate system, and possible tunneling routes.  $V$  denotes the hopping integrals between different subsystems and  $G$  denotes the Green's function. (b) The potential step model for tunneling through a molecule.

valuable discussion of important factors contributing to tunneling currents. However, it is possible to go one step further, and connect the discussion of Ref. 8 to features of a more general Green's-function approach.

In this paper, we shall investigate the role and origins of the phase difference of the wave function in through-molecule and through-vacuum channels. We especially attempt to make a mapping from a straightforward transmission model of an advancing wave through a barrier to a more abstract Green's-function-based scattering approach. In connection with the latter approach, we discuss the role of imaginary and real parts of the complex retarded Green's function in analyzing different tunneling channels. That kind of analysis enables one to distinguish the role of phase shifts in possible tunneling channels, which may go through resonant states or forbidden gaps.

## II. COMPARISON OF A SIMPLE BARRIER MODEL TO A GREEN'S-FUNCTION APPROACH

In the following, we consider two different *generic models* for tunneling of electrons across a spatial gap between a metal surface and the tip. The approaches take into account the most salient features of an adsorbate molecule. First, we consider tunneling through a potential step with one or two potential wells as in Fig. 1. The step models the vacuum between an STM tip and a metal substrate, and the wells (with bound states) represent an adsorbate molecule. Second, tunneling is considered in a more general and formal way by inspecting the Lippmann-Schwinger equation and the related equations for the tunneling current. We will see that the two approaches are useful in considering interference between wave functions for different tunneling channels. In addition, they give an insight into the physical significance of the real and imaginary parts of the adsorbate Green's function, and they explain why the local density of states does not always

correlate with the contrast of the STM image.

The basic model for both cases is given in Fig. 1(a), which shows the TA and TS routes for tunneling. If the amplitudes of the two waves are of the same order of magnitude, it is the phase difference which determines the total amplitude of the scattering wave and thus the magnitude of the tunneling current. Figure 1(b) shows the potential barrier model, where there is a single or double well to model an adsorbate molecule. The incoming electron is modeled as a plane wave  $\psi_i = \exp(ikx)$ , the reflected wave is  $\psi_r = R \exp(-ikx)$ , and the transmitted wave is  $\psi_t = T \exp(ikx)$  (this model can be found in elementary books on quantum mechanics, such as Ref. 9). The transmission coefficient  $T$  can be written in a complex polar form

$$T = |T| e^{i\varphi},$$

and the tunneling current is proportional to  $|T|^2$ . If we adapt a denotation  $\varphi_s$  and  $\varphi_a$  for the TS and TA phases, respectively, the phase difference for the two channels is  $\Delta\varphi = \varphi_a - \varphi_s$  and the total tunneling current is  $j \propto |T_a + T_s|^2$ .

The current density for a single well shows a high peak at the neighborhood of the eigenenergy of the single well. It is seen that there is no phase difference,  $\Delta\varphi$ , between the through-space and through-molecule waves below the resonance, but there is a half wavelength difference above the resonance. In very simplistic terms, this phase change can be explained by the fact that a resonance level corresponds to an energy where the width of well is a multiple of half a wavelength. This causes a change of sign for the wave function when crossing over a resonance. Thus, for a well with only one single resonance, the TS and TA waves should weaken each other at energies above the resonant level. However, at the very neighborhood of the resonance, TA tunneling is so dominant that the interference effect should be quite negligible. But further away from the resonance, the amplitudes of the two channels match better, and interference should weaken the total current.

A double well was used to model a diatomic molecule standing perpendicular to the surface. In the case of a double well, there is a finite gap between the two molecular energy levels. In this case, there are two maxima of the current density in the neighborhood of the resonant states (see Fig. 2). Below the lower resonance, there is no phase difference between the two channels, and  $\Delta\varphi$  approaches  $2\pi$  above the upper resonance. At the energies between the resonances, the phase difference is  $\Delta\varphi \approx \pi$ . This result suggests that this one-dimensional model does not predict any change of contrast at energies within the gap. Also, the phase shifts at the molecular energy levels suggest that the change in contrast is only possible when the energy of the tunneling electrons is varied in the neighborhood of resonances.

This model is, however, a one-dimensional barrier model. A more realistic approach can be reached with Green's-function methods. We can formulate the effect of the adsorbate to the wave function of a tunneling electron in the form of the Lippmann-Schwinger equation,<sup>10</sup>

$$|\psi^+\rangle = |\phi\rangle + G^+ V |\phi\rangle = |\phi\rangle + G^0 T |\phi\rangle, \quad (1)$$

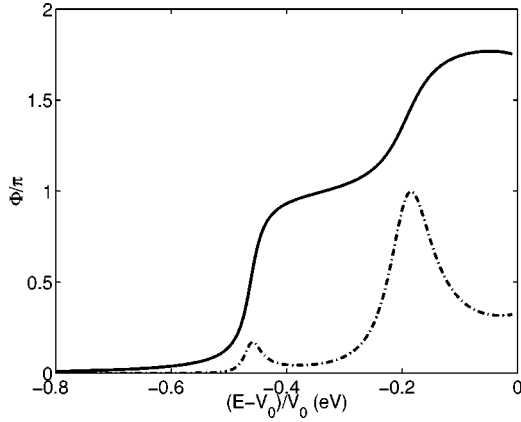


FIG. 2. The energy-dependent phase difference between TA and TS waves for the potential step model with a double well (solid line). The dash-dotted line indicates the current density through a double well (in arbitrary units).

where  $\phi$  refers to the unperturbed wave,  $\psi^+$  to the wave in the presence of the adsorbate,  $G^0$  is the Green's function for the unconnected system,  $G^+$  is the retarded Green's function (in the presence of the adsorbate),  $V$  is the perturbation potential due to the adsorbate, and  $T$  is the transition operator between the tip and the substrate. Dyson's equation connects the Green's function of an unperturbed system,  $G^0$ , and of a perturbed system  $G^+$  (see, e.g., Ref. 10):

$$G^+ = G^0 + G^0 V G^+.$$

Applying Dyson's equation to the Lippmann-Schwinger equation, we see that the retarded Green's function is related to the transition matrix by

$$T = V + V G^+ V. \quad (2)$$

Denoting the orbitals of the tip with index  $t$  and the orbitals of the substrate with index  $s$ , we obtain a formula for the tunneling current which is independently suggested by Todorov *et al.*<sup>3</sup> and Pendry *et al.*<sup>4</sup>

$$j = \frac{2\pi e}{\hbar} \int [f(E) - f(E + eV_b)] \times \text{Tr}[\rho_{s',s}^0(E) T_{st}(E) \rho_{tt'}^0(E) T_{ts'}^\dagger(E)] dE, \quad (3)$$

where  $\rho^0$  is the density-of-states matrix for the noninteracting system (without adsorbate), and  $T$  is the transition matrix between the eigenstates of the tip and the eigenstates of the substrate. The presence of the adsorbate is taken into account in the transition matrix,

$$T_{st} = V_{st} + V_{sa} G_{ab}^+ V_{bt}, \quad (4)$$

where  $V$  is the matrix for hopping integrals of tip-adsorbate-substrate interactions. From the formula above, one can derive a differential conductance<sup>3</sup> (see also, e.g., Ref. 11 for the Landauer-Büttiker formula)

$$\sigma \propto T_{st} T_{ts}^\dagger \rho_s(\mathbf{r}, E),$$

which is not simply proportional to the LDOS, since the  $T$  matrix is strongly dependent on the chemical composition of the sample and thus on the position of the tip.

The real and imaginary parts of the Green's function in the  $T$  matrix [Eq. (4)] reveal some information about the nature of tunneling and current flow. Generally, the Green's function presents a response function to an external perturbation. The real and imaginary parts of a response function are related to fluctuation of a physical observable and power dissipation, respectively.<sup>12</sup> In this special case of the Green's function, dissipation is related to a transition between eigenstates of the system, since the imaginary part of the Green's function gives the eigenspectrum. Fluctuation, on the other hand, is a manifestation of a nonstationary wave or an evanescent solution to the time-dependent Schrödinger equation. Thus, a purely nonimaginary Green's function appears in the case of tunneling through a forbidden band of the spectrum where the tunneling electron sees the molecule effectively as a potential barrier.

If we consider tunneling from the tip to the substrate, we need a Green's function connecting the adsorbate and the substrate. If there is weak coupling between the two systems, the first-order approximation of Dyson's equation gives a good starting point for the analysis:

$$G_{sa}^+ \approx G_{ss}^0 V_{sa} G_{aa}^0,$$

where we assume that the adsorbate ( $a$ ) is completely disconnected from the substrate ( $s$ ) in the case of the unperturbed system. Thus, if we are to model tunneling from the tip to the substrate, we can investigate the behavior of such combinations as [see Fig. 1(a)]

$$G_{sa}^+ V_{at} |\phi_t\rangle \approx G_{ss}^0 V_{sa} G_{aa}^0 V_{at} |\phi_t\rangle.$$

In a tight-binding basis, the matrix elements of the perturbation potential  $V$  depend on distance and orientation of the molecule but are constant in energy. We may also assume that the substrate matrix elements of the Green's function do not change dramatically in the neighborhood of the Fermi energy. Thus, we are interested in phase changes in the adsorbate matrix elements of the Green's function  $G_{aa}^0 = |G_{aa}^0| e^{i\varphi_{aa}}$ . A change in the phase  $\varphi_{aa}$  is seen as a change in the phase of the wave function of the tunneling electron, and this may result into a change of contrast of a molecule in an STM image.

We can start constructing the total Green's function from a Green's function of a single atom with one valence level  $E_a$ ,

$$G_{aa}^0 = \frac{1}{E - E_a + i\eta} = \frac{\exp(i\varphi_{aa})}{\sqrt{(E - E_a)^2 + \eta^2}}, \quad (5)$$

where  $\varphi_{aa} = \arctan[-\eta/(E - E_a)]$  is the phase of the Green's function. It is easy to see that the absolute value of the Green's function is essentially nonzero only in the neighborhood of the eigenstate  $E = E_a$  and the parameter  $\eta$  determines the width of the resonance. Furthermore, the phase changes from  $\varphi_{aa} = \pi$  via  $\varphi_{aa} = -\pi/2$  to  $\varphi_{aa} = 0$  as one goes from energies below the resonance to energies above the

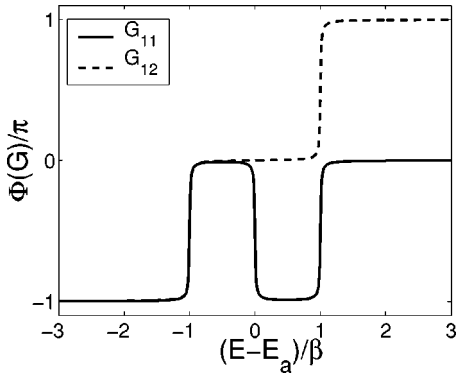


FIG. 3. The energy-dependent phases of the matrix elements of the Green's function for a two-atom molecule with  $s$  orbitals (a) gives the phase for a diagonal element of the Green's function, and (b) for an off-diagonal matrix element. The parameter  $\beta$  is the hopping integral between the  $s$  orbitals.

resonance. Thus, there is a sudden reversal of the phase of the wave function of a tunneling electron. Since we have implicitly assumed an  $s$ -orbital model, we know that the transition matrix  $T_{sa} = V_{sa}$  for the TS current is negative, i.e., there is a phase shift of  $\pi$  for a TS wave. Thus, there is no phase difference below the resonance and a half wavelength difference above the resonance. Adding up all these results, a one-to-one correspondence with the potential barrier model is found.

Next, we model a two-atom molecule using two atoms with one orbital each. The same on-site matrix element of the Hamiltonian  $V_{11} = V_{22} = E_a$  is chosen for both the atomic orbitals, and a hopping integral  $V_{12}$  between the orbitals is used. The matrix elements  $G_{11}^0$ ,  $G_{22}^0$ , and  $G_{12}^0$ , and their phases can be calculated, e.g., using Dyson's equation. In Fig. 3 one can see that the diagonal and off-diagonal elements of the Green's function have somewhat different behaviors. Now, we should start with  $G_{12}^0$  which is required when we consider tunneling going through a route tip  $\rightarrow$  atom 1  $\rightarrow$  atom 2  $\rightarrow$  substrate. This might be a simplified model for an adsorbate molecule standing perpendicular to the substrate surface, such as CO.<sup>13</sup> In fact, CO is heteronuclear and also should be modeled with a basis set of at least eight orbitals. Nevertheless, the same idea of hopping through the two atoms applies for the molecule. To make a comparison to the barrier model, this is essentially the case of the potential barrier with two potential wells, which we considered earlier. Two resonant maxima are found, now at energies  $E_a \pm V_{12}$ , and two phase reversals take place, both at the resonances just as in the case of the double well in a potential barrier.

This result for the off-diagonal elements of the Green's function indicates that there may be a change in contrast when crossing over a resonant state, but it does not encourage finding a change in contrast within a gap between HOMO and LUMO states. However, considering the diagonal elements of the Green's function of the molecule gives quite a different result. Figure 3 shows that the phase of a diagonal element  $G_{11}^0 = G_{22}^0$  is reversed not only at the resonances but also *in the middle of the gap* between the eigen-

levels of the molecule. Thus, if tunneling takes place through a route tip  $\rightarrow$  atom 1  $\rightarrow$  substrate, a sudden change from a constructive interference to a destructive interference may take place as states at different sides of the Fermi energy are probed. This tunneling channel is likely for a molecule which lies parallel to the surface, such as  $O_2$ .<sup>14</sup> On the other hand, this might be a possible channel also for a perpendicular adsorbate especially when STM is probing the positions not at the molecule but in its neighborhood. This kind of route gives a potential explanation for dark halos in STM images around a molecule such as  $O_2$  (parallel) (Ref. 14) and CO (perpendicular) (Ref. 13).

### III. TODOROV-PENDRY APPROACH AND THE QUALITATIVE ANALYSIS BY SAUTET

The Todorov-Pendry Green's-function approach can be rather directly compared to the qualitative approach by Sautet.<sup>8</sup> In Sautet's approach, the substrate and the STM tip are described by two semi-infinite chains. The hopping integral for direct coupling between the tip and the substrate is denoted by  $\gamma$ . The adsorbate is modeled with an atom with resonant states at energies  $\omega_i$ , and the hopping integrals from the corresponding orbitals to the substrate and the tip are denoted by  $\alpha_i$  and  $\beta_i$ , respectively.

From these ingredients an effective coupling between the tip and the substrate can be constructed:

$$\Gamma = \gamma + \sum \frac{\alpha_i \beta_i}{E_f - \omega_i}.$$

In addition, the energy level of the orbital at the surface site of the adsorbate is shifted as

$$e^* = e + \sum \frac{\alpha_i^2}{E_f - \omega_i},$$

where  $e$  is the unperturbed energy level of the surface site. It can be shown that there are three major qualitative trends that can be seen from these formulas:

(i) The shift in the energy of the surface site diminishes the density of states of the surface at the resonant state of the adsorbate, and this decreases the current to the substrate site.

(ii) If the adsorbate has a resonance in the vicinity of the Fermi energy, there is a large and dominating TA current.

(iii) The signs of  $\alpha$ ,  $\beta$ , and  $E_f - \omega$  as compared to the sign of  $\gamma$  determine whether the TS and TA currents are in the same or the opposite phase. Thus, the interference effects are important if TS and TA currents are of the same order of magnitude. There are two factors which may lead to this: either the tip may be in such a position that  $\beta$  has a suitable value, or the nearest resonance is so far from the Fermi energy that the TA current is moderate.

The formulas given by Sautet have similarities to the present Green's-function formalism. The effective coupling between the tip and the substrate seems to be a direct counterpart to the equation for the transition matrix of Eq. (4). The first term is clearly the direct tip-substrate coupling term  $\gamma$ , and the second term is a sum over products of tip-adsorbate and substrate-adsorbate hopping integrals with the

adsorbate Green's-function terms. However, there seem to be two main differences. First, the  $\Gamma$ -term contains the unperturbed adsorbate Green's function, whereas Eq. (4) contains the Green's function for the connected system. Second, there is the density of states for the unperturbed surface in the Todorov-Pendry formula Eq. (3), whereas Sautet deals with a perturbed surface site. Thus, if the two approaches are equivalent, they seem to have different regrouping of terms.

The division into TS and TA currents becomes more transparent in the Todorov-Pendry formula if the transition matrix  $T$  is written in terms of the hopping integrals  $V$ . Let us extract the terms

$$T_{ts}^{TS} = V_{ts} + V_{ts} G_{sa}^+ V_{as} = V_{ts} (1 + G_{sa}^+ V_{as}).$$

Note that the inner indices are summed over all the orbitals of either the substrate or the adsorbate. Then recall that the local density of states can be written<sup>3</sup>

$$\rho_{ss'}^0 = -\frac{1}{\pi} \text{Im}(G_{ss'}^0) = \frac{\eta}{\pi} G_{ss''}^{0+} G_{s''s'}^{0-}.$$

From these equations, we can readily see that

$$T_{ts}^{TS} \rho_{ss'}^0 T_{st}^{TS\dagger} = \frac{\eta}{\pi} V_{ts} (1 + G_{sa}^+ V_{as}) G_{ss''}^{0+} G_{s''s'}^{0-} (1 + V_{sa} G_{as}^-) V_{st}.$$

Utilizing Dyson's equation the last form becomes

$$T_{ts}^{TS} \rho_{ss'}^0 T_{st}^{TS\dagger} = \frac{\eta}{\pi} V_{ts} G_{ss''}^+ G_{s''s'}^- V_{st} = V_{ts} \rho_{ss'} V_{st}^\dagger,$$

which corresponds to the TS current in Sautet's formula, where the hopping of electrons takes place at *perturbed* states of the substrate. Thus, we can attribute  $T^{TS}$  to through-space tunneling and  $T - T^{TS}$  to through-adsorbate tunneling.

Correspondingly, the same kind of analysis can be done to the TA current. If we define

$$T_{ts}^{TA} = V_{ta} G_{ab}^+ V_{bs}$$

following the same train of thought as in the case of the TS current, we obtain

$$T_{ts}^{TA} \rho_{ss'}^0 T_{st}^{TA\dagger} = \frac{\eta}{\pi} (V_{ta} G_{ab}^+ V_{bs} G_{ss''}^{0+}) (G_{s''s'}^{0-} V_{sb} G_{ba}^- V_{at}).$$

But according to Dyson's equation, the order of the unperturbed and perturbed Green's functions can be changed, and thus we obtain

$$\begin{aligned} T_{ts}^{TA} \rho_{ss'}^0 T_{st}^{TA\dagger} &= \frac{\eta}{\pi} (V_{ta} G_{ab}^{0+} V_{bs} G_{ss''}^+) (G_{s''s'}^- V_{sb} G_{ba}^- V_{at}) \\ &= (V_{ta} G_{ab}^{0+} V_{bs} \rho_{ss'} V_{s't} G_{ba}^- V_{at}). \end{aligned}$$

And for the cross terms, which in fact belong to through-adsorbate terms, we obtain

$$T_{ts}^{TA} \rho_{ss'}^0 T_{st}^{TS\dagger} = (V_{ta} G_{ab}^{0+} V_{bs} \rho_{ss'} V_{s't}).$$

Thus, the current can be entirely described in terms of perturbed substrate and unperturbed adsorbate and tip.

We can also analyze whether the Green's-function approach supports the proposition that the adsorbate decreases the local density of states at the substrate, and thus the TS current. For that we can utilize Dyson's equation, again in order to compare  $G_{ss}^0$  and  $G_{ss}$ . The relation between the two is

$$G_{ss} = G_{ss}^0 + G_{ss}^0 V_{sa} G_{as},$$

since  $V_{ss} = 0$ . In addition,

$$G_{as} = G_{aa}^0 V_{as} G_{ss} \approx G_{aa}^0 V_{as} G_{ss}^0,$$

since  $G_{as}^0 = 0$ . Thus, we can express the variation of the substrate Green's function  $\delta G_{ss}$  in terms of the unperturbed Green's functions and the hopping integrals:

$$\delta G_{ss} = G_{ss}^0 V_{sa} G_{aa}^0 V_{as} G_{ss}^0 = G_{aa}^0 |V_{as}|^2 (G_{ss}^0)^2.$$

This equation, as such, does not directly show the sign of the change of the local density of states. However, if we assume a chain model for the substrate, it is well known that the Green's function can be written in a form<sup>15</sup>

$$G_{ss}^0(E) = b^{-1} \exp(i\theta),$$

$$\cos(\theta) = \frac{E-a}{2b},$$

where  $a$  is the middle of the band, and  $4b$  is the width of the band. In addition, it can be seen from Eq. (5) that the phase of the adsorbate Green's function is  $\varphi = -\pi/2$  at the resonance. Thus, we can write

$$\delta G_{ss} = \frac{|V_{as}|^2}{b^2 \sqrt{(E-E_a)^2 + \eta^2}} \exp[i(\varphi + 2\theta)]$$

and

$$\delta \rho_{ss} = -\frac{1}{\pi} \text{Im}(\delta G_{ss}) = \frac{-|V_{as}|^2}{b^2 \pi \sqrt{(E-E_a)^2 + \eta^2}} \sin(\varphi + 2\theta). \quad (6)$$

Let us look at the variation at the resonance, where the absolute contribution is largest. In the middle of the band we have  $\varphi + 2\theta \approx \pi/2$ , and thus  $\sin(\varphi + 2\theta) = 1$  and  $\delta \rho < 0$ . On the other hand, at each end of the band  $\varphi + 2\theta \approx -\pi/2$ , and thus  $\sin(\varphi + 2\theta) = -1$  and  $\delta \rho > 0$ . Thus, we can conclude that the assumption of a decreasing density of states is correct near the middle of the band, but it fails with increasing intensity the closer the resonance is to the edges of the band.

This analysis is, in fact, not restricted to the linear-chain model. A general equation for the change of the LDOS has the same form as Eq. (6), but the modulus of the change has a different energy dependence. It is also clear that in the middle of the band, where the imaginary part of the substrate Green's function is large and the real part is small, the angle  $2\theta \approx \pm \pi$ , and thus an adsorbate resonance, causes a decrease in the LDOS. In the opposite case, where the real part is relatively large,  $\theta$  is either 0 or  $\pi$ , and thus  $2\theta \approx 2\pi$ .

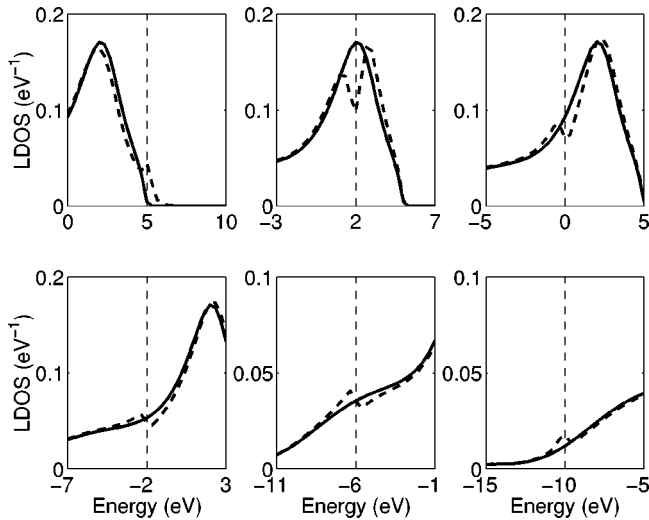


FIG. 4. LDOS of a metal atom on a clean fcc(111) surface (solid lines) and with an adsorbate atom on top (dashed lines). The adsorbate atom has one  $s$  orbital overlapping with the substrate wave function. The on-site energy of the adsorbate atom, marked with vertical lines, is varied with respect to the Fermi energy at 0 eV.

Thus, the change in the LDOS is positive. This kind of situation takes place outside of or close to the edges of the band.

We have verified these conditions for an fcc(111) surface with an adsorbate at top and hollow sites. We did not only make the calculations with a hydrogenlike atom with one  $s$  orbital, but found the same phenomenon for an atom with one  $s$  and three  $p$  orbitals. In Fig. 4 we show the change of the LDOS in the presence of an adsorbate on a top site, but the similar behavior is seen for the hollow site. For both adsorption sites, the resonant state of an adsorbate decreases the LDOS of the substrate more clearly the closer the state is to the middle of the band. Near the edges of the band the adsorbate causes an extra peak to the LDOS. It should be noticed, however, that the total number of electron states must be conserved, and thus a drop at some energy must be compensated by a peak somewhere else, and vice versa, which can also be seen in Fig. 4. One should be able to verify this by changing the substrate material. If one uses a substrate where the adsorbate has a resonant state rather close to the middle of the  $sp$  band, it should cause a halo in the LDOS which, obviously, should be seen as a halo around the adsorbate, since the resonant state itself strongly increases the TA current. On the other hand, if the resonant state is relatively close to the edge of the band, there should be an increase in the LDOS of the substrate, which should emphasize the surroundings of the adsorbate.

#### IV. AN EXAMPLE: O<sub>2</sub> ON Ag(100)

In the following, we consider an experimental case of O<sub>2</sub> molecules on an Ag(100) surface, where a change from dark STM images of a molecular adsorbate turns bright as the bias voltage is changed from positive to negative. We attempt to analyze the contrast change theoretically by considering the relevant tunneling channels and matrix elements of the Green's function within the adsorbate, and between the ad-

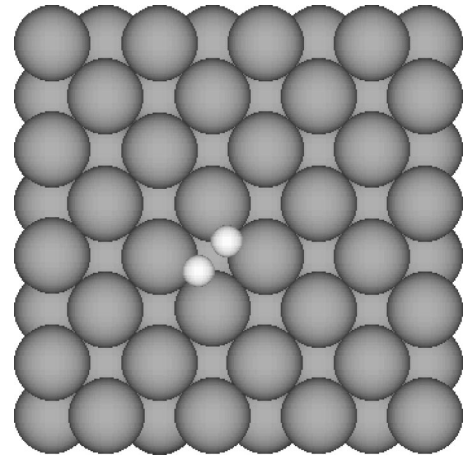


FIG. 5. A real-space image for the proposed adsorption site of an O<sub>2</sub> molecule on Ag(100).

sorbate and the substrate. It is confirmed by a molecular-dynamics simulation that a single molecule tends to adsorb at a fourfold hollow site pointing towards the [110] direction.<sup>16</sup> In the theoretical analysis, we assume that the molecules do not interfere with each other's electronic structure, so that we can consider a single molecule, only.

In the theoretical calculations, we model the substrate as a slab of six layers with 32 atoms at each layer. The microscope tip is a five-atom pyramid at the bottom of the slab, and the molecule is situated on the top of the slab, as shown in Fig. 5. Thus, the slab acts simultaneously as a substrate and a tip holder. Lees-Edwards periodic boundary conditions<sup>17,18</sup> are utilized to model the horizontal motion of the microscope tip, and the tunneling current is calculated across the simulation of the cell boundary. The image calculation simulates the constant current mode, which is maintained by controlling the height of the simulation cell. We use the method described in Ref. 19 to calculate the relevant elements of the Green's function of the tip-adsorbate-substrate system. The matrix elements of the substrate  $s$  orbitals are approximated to the fourth moment (see also Ref. 20).

In the experimental image (Fig. 6), we can see a group of O<sub>2</sub> molecules adsorbed on the silver surface (see the experimental details in Ref. 16). At a negative bias voltage  $U = -1.06$  V, the molecules can be seen as bright elliptical pat-

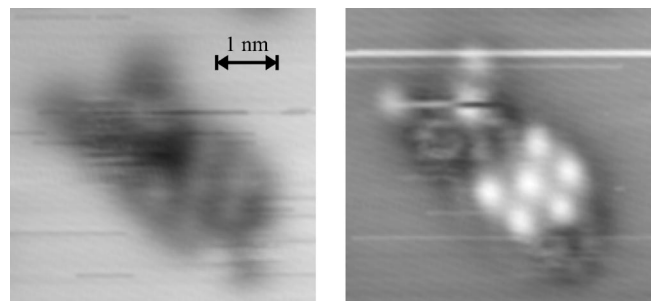


FIG. 6. Two experimental STM images of a cluster of O<sub>2</sub> molecules on an Ag(100) surface. On the left, the bias voltage is +1.06 V, and on the right, the bias voltage is -1.06 V.

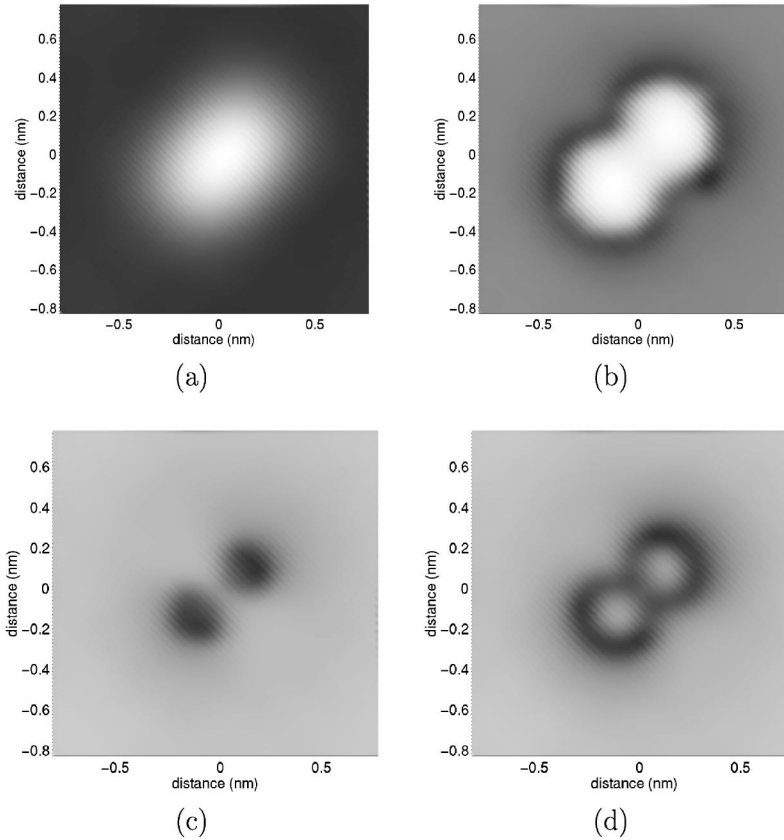


FIG. 7. Calculated STM images for different bias voltages:  $U = -1.00$  V (a),  $U = -0.50$  V (b),  $U = +0.50$  V (c), and  $U = +1.00$  V (d).

terns on the gray background. As the bias voltage is reversed to  $U = +1.06$  V the contrast is changed so that the layer of the molecules is seen as a dark area. The new image is not, however, a right negative image of the original. Rather, it seems that while the molecules themselves become rather invisible from the background, it is the surface between the molecules that is seen as darkest. This suggests that there might be destructive interference between tunneling waves to the molecule and the surface area between the molecules.

In our calculations, we find a rather narrow energy range for a contrast change. We start from  $-1.0$  V, where the molecule is seen as a bright protrusion, quite like the experiments. A dramatic change of the image is found between  $-0.5$  V and  $+0.5$  V from a bright elliptical pattern to a dark pattern and then towards a brighter pattern again. In Fig. 7, we show a set of calculated images for a single molecule, where this contrast change is seen. In the bias voltages near  $+1.0$  V we find, in fact, that the surroundings of the molecule have a dark contrast in comparison with the molecule and the surface. This matches quite well the experimental images, where the molecules are seen as rather light gray spots surrounded by a darker area. Obviously, lots of details of the LDOS are lost in our approximations, and thus an exact match with experimental results cannot be expected. In addition, the structure and the distance of the tip affect the image. Despite these shortcomings, we find a very clear qualitative accordance with the experiment, in this special case.

In order to make a simplified analysis of tunneling for this case, we have to consider how the molecular orbitals behave

in the adsorption. It is obvious that there is a strong overlap between one of the  $\pi$  orbitals of  $O_2$  with the substrate, and this evidently breaks up the degeneracy of the  $\pi$  orbitals. Thus, it is obvious that the  $p_z$  orbitals perpendicular to the surface are rather independent from each other for the adsorbed molecule. Because they extend rather far from the nucleus of the atom towards the vacuum, they are mainly responsible for the TA current. The relevant elements of the Green's function are the diagonal elements  $G_{zz}$  and the off-diagonal elements between the molecule ( $z$ ) and the substrate ( $\sigma$ ),  $G_{\sigma z}$ .

One must be careful in analyzing the phase differences between different tunneling channels, since the phase of the Green's function does not directly give the phase difference  $\Delta\varphi$  between the specific channel and the direct TS channel. Rather, one must compare the phases of the direct TS term  $V_{ts}$  of the transition matrix and those of terms such as  $V_{ta}G_{aa}V_{as}$ . In the present calculations, direct tunneling always has the phase  $\pi$  since the hopping integral  $V_{ts}$  is negative ( $-$ ). In the case of TA tunneling through the  $p_z$  orbital, we consider a combination  $V_{tz}G_{zz}V_{zs}$ . First, the hopping integral  $V_{tz}$  is negative, since  $p_z$  has a positive upward lobe. Second, the hopping integral  $V_{zs}$  is positive due to the negative lobe of the  $p_z$  orbital. Thus, the total phase difference  $\Delta\varphi$  to the direct TS component is the phase of  $G_{zz}$  [see Fig. 8(a)]. In the case of TS tunneling through the  $p_z$ , we must consider a term  $V_{t\sigma}G_{\sigma z}V_{zs}$ . The phase of the hopping integral between the tip and the substrate,  $V_{t\sigma}$ , is negative. Then again  $V_{zs}$  is positive, and thus it is the Green's function  $G_{\sigma z}$

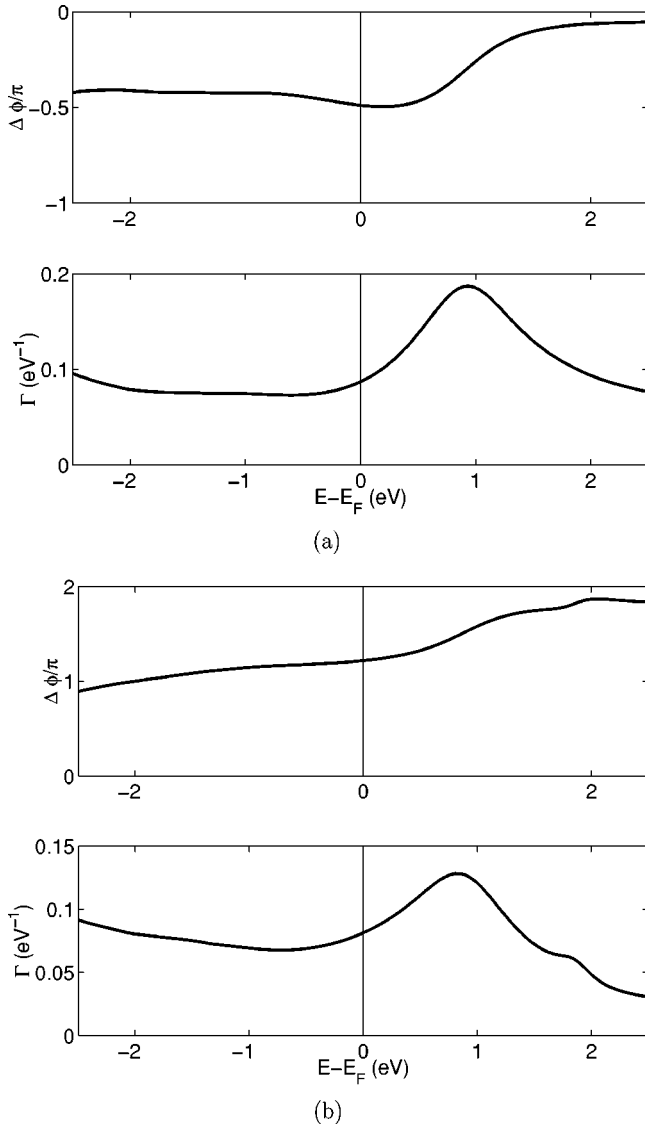


FIG. 8. The phase difference,  $\Delta\phi$ , between a chosen tunneling channel and the direct TS channel, and the absolute value,  $\Gamma$ , of the corresponding matrix element of the Green's function. The figure shows  $\Delta\phi$  and  $\Gamma$  related to the diagonal element,  $G_{zz}$ , of an oxygen  $p_z$  orbital (a), and the off-diagonal element,  $G_{\sigma z}$ , between the  $p_z$  orbital and the  $s$  orbital of a neighboring silver atom (b). The Fermi energy is at 0 eV.

which directly determines the phase difference,  $\Delta\phi$  [see Fig. 8(b)]. Therefore, for both tunneling channels the phase of the Green's function directly determines the nature of the interference between the channels and the direct TS tunneling.

Figure 8 shows two important features for these matrix elements. First, both matrix elements of the Green's function change from zero phase difference to nonzero phase difference when changing from energies above the Fermi energy (negative bias voltages) to energies below the Fermi energy (positive bias voltages). Second, the absolute value of both elements of the Green's function is decreasing from about 1.0 eV towards  $-1.0$  eV, i.e., from bias voltage  $-1.0$  V towards  $+1.0$  V. In the case of  $G_{\sigma z}$ , the phase change is almost complete from zero to  $\pi$ , whereas the phase change

of  $G_{zz}$  is much more moderate. Obviously, this is consistent with the fact that the molecules themselves do not appear dark at  $+1.0$  V. Rather, it is the substrate around the molecule where there are factors in opposite phases at positive voltages. This effect is still seen in calculations at  $+1.5$  V where the molecule itself is again rather bright but the surrounding is dark. Unfortunately, such a high bias voltage tends to destroy the molecular clusters, and thus this behavior cannot be confirmed experimentally. To conclude, the calculated images are in accord with the experimental ones, and the contribution of different tunneling channels to the contrast change can be relevantly traced and analyzed by considering the matrix elements of the Green's function.

## V. CONCLUSIONS AND DISCUSSION

There are two main objectives for the present study. First, we have demonstrated that different methods to model tunneling can be mapped to each other. Second, we point out factors that affect the contrast of an adsorbate molecule on a solid surface. When discussing the generic models, we showed that an easily conceivable potential barrier model is consistent with a more abstract scattering method, which is constructed in terms of the Green's functions and is based on the Lippmann-Schwinger equation. The scattering method is the theoretical basis for the Todorov-Pendry approach which is applied in the example system of this paper. It has been shown in Refs. 3 and 4 that the Todorov-Pendry approach is a generalization to models where the change in bias voltage is treated in the framework of linear-response theory. In the present study, we also demonstrate a close connection between the Todorov-Pendry approach and the analysis by Sautet.<sup>8</sup>

A few general conclusions can be drawn from the potential barrier and the Green's-function approaches. First, there is a strong current through an unoccupied resonant state. This produces a bright STM image of the adsorbate. Second, tunneling above a resonance makes a phase shift of  $\pi$  as compared to tunneling below a resonance. Further off the resonance in terms of energy, the amplitude of the tunneling wave function is small, and the adsorbate is seen as a potential barrier. However, a phase shift may cause a destructive interference, which means a dark STM image. Third, in a gap between resonant levels, there is no phase change in a one-dimensional model. However, the Green's-function formalism for a diatomic molecule reveals that the diagonal and off-diagonal elements of Green's functions have a different phase behavior in the gap. Thus, the final contrast may depend on, e.g., the position of the tip with respect to the adsorbate.

Unfortunately, a general theory for the contrast change cannot be derived in very simple terms, since the relative amplitudes of transmission through different tunneling channels depends on the details of the electronic structure. Thus, for real adsorbate-substrate systems a more complete calculation of tunneling currents must be done. Nevertheless, this kind of simple analysis makes it easier to interpret both



experimental and theoretical STM images. This has been demonstrated by applying the Todorov-Pendry approach to oxygen on silver, and drawing conclusions from the behavior of the Green's function of the system and the phase factors of different tunneling routes.

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