A simple interpretation of quantum mirages

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(March 21, 2022)

Pacs: 73.20.Hb, 73.23.Ps
Keywords: Mirages, Quantum corrals

The electronic structure of systems with adsorbed impurities on noble metal surfaces should depend both on the type and the geometric arrangement of the adsorbed atoms. In particular, the effect of single transition-metal impurities and also of dimers on the (111) surface of gold has been studied recently with scanning tunneling microscopy [1,2]. Previously, closed loops of impurities had been shown to confine the surface state wavefunctions of Cu(111), producing what are now called "quantum corrals" [3]. In an interesting new experiment the electronic structure surrounding an adsorbed magnetic atom could be projected into a remote location on the same surface [4]: a Kondo "signature" in the tunneling spectrum of a cobalt atom located on one focus of an elliptical corral was observed as a mirage on the other focus. This possibility raises many theoretical questions, the first one being the relation between this quantum system and classical image projection. Other questions regarding the experimental setup are: How does the appearance of a mirage depend on the surface type, on the adsorbed atom type, on the shape of the corral, etc? The fact that the (111) surface of noble metals presents a symmetry gap at the Γ point and a surface state at about 0.5 eV below the Fermi energy, uncoupled from the bulk states, seems of course fundamental. For the other questions one must take a closer look and this is the purpose of the present paper. It must be emphasized, however, that we are not attempting a full theoretical description of the experiment but rather a simplified approach to the previous questions.

We start by assuming a model Hamiltonian for the interaction of one adsorbed atom with the surface state of the metal, using the following approximations:

1. The substrate is represented by a bidimensional array of atoms arranged in a triangular lattice, representing the (111) surface of copper, the only effect of the bulk material being to provide the position of the Fermi level. A tight-binding model with one orbital per site and first neighbor interactions is used to represent the atomic interactions within the surface. It gives an energy band between $E_0 - 6t$ and $E_0 + 3t$, that shows a parabolic shape close to the Γ point, as does the surface state in the (111) surface of noble metals. The self-energy of the copper atoms ($E_0$) is set to zero and the nearest neighbor hopping parameter to $t = 1eV$, a value in the appropriate range for the s band of copper. Since the surface state at Γ is approximately 0.5 eV below the Fermi level in this case, the resulting Fermi energy is $E_F = -5.5eV$

2. The corral is simulated by setting a very large value of $E_0$ for the limiting atoms, or else by just the absence of atoms beyond the corral limits. We have tried other boundary conditions and found that there is no qualitative difference in the results. From previous work [4] we know that the surface state develops when the size of the unperturbed surface region is larger than about 10 lattice spacings, which limits the size of the smaller ellipses to be considered.

The particular elliptical corral we study here, as the experimental one [4], has semiaxis $a = 26d = 70A$, $d$ being the nearest neighbor distance in copper, and eccentricity $e = 0.5$ so that it encloses around 2300 copper atoms. Diagonalization of the tight-binding matrix gives information on the wavefunctions, in particular for the relevant levels close to the Fermi energy. Fig. 1 shows the charge density for four such levels, from the 39th to the 42nd eigenfunctions.
The oscillations observed in the STM topography are expected to be related to the maxima and minima of these charge densities. It can be seen that functions number 39 and 42 are both quite similar to the pictures in Ref.5 but one has pronounced maxima very near the foci of the ellipse while the other has the maxima far away from them.

3. For simplicity, the adsorbed atom is assumed to be on the atop position, therefore interacting with only one of the copper atoms. In the experimental case the adsorbed atom is cobalt, which is strongly magnetic. When cobalt films or clusters are deposited on noble metals, a mean field approach to the electronic structure would postulate that due to a complicated many-body process the up and down bands separate, one of them being completely filled up while the other one straddles the Fermi level so as to be partially occupied. Therefore, the narrow minority band acts as an impurity with self-energy close to the Fermi energy. In the present case we only consider the minority level and its interaction with the corresponding surface level; the complicated process is therefore replaced by a resonant model in which the fine-tuning of the energies is fundamental. This resonant model can also apply to the Kondo resonance at $E_F$. An atom having a self energy very close to the Fermi energy is placed atop one of the copper atoms and the interaction between them is represented by a hopping constant $t'$. The value of this parameter is very important in the model; if it is too large it leads to a sizable distortion of the surface wavefunctions which is not the case experimentally. The STM pictures in Ref.5 show that one adsorbed cobalt atom inside the ellipse does not change the topography drastically. If $t'$ is too small its effect is of course negligible. The value $t' = 0.05 eV$ produces what we believe to be an effect related to the mirage, that is, a splitting of the correct magnitude of just the level with energy $E_F$, to which the atop atom is tuned. The wavefunctions in a tight-binding model are obtained as a linear combination of the atomic orbitals and elementary considerations show that the splitting is directly proportional to $t'$ and to the magnitude of the particular coefficient corresponding to the copper atom that is connected to the adsorbed atom, and inversely proportional to the mistuning of the energy.

Some results obtained from this model Hamiltonian are shown in Fig. 2. Fig. 2a shows a projection of the probability density from state 42 of Fig. 1, while Figs. 2b and 2c are the probabilities of the two split levels for the case of an adsorbed atom placed atop the site $x = 12d$ where the wavefunction is maximal, near a focus of the ellipse. A similar plot is obtained when the adsorbed atom is placed in a position where there is a smaller secondary maximum, as for example $x = 7d$. The only difference between the two situations is the larger energy splitting in the first case ($8 meV versus 5 meV$). The difference between Figs. 2b and 2c is a consequence of the slight mistuning of the adatom self-energy and the Fermi energy. The surface topography will remain unchanged by the interaction, as the sum of the split wavefunctions is almost identical to the original one, but a spectrum scanning the density of states will find a dip at the Fermi level of the order of the energy splitting, less than 0.01 eV. This dip will appear in the local densities of states proportionally to the corresponding coefficients and therefore will be larger at the foci. A similar calculation on function 41, with a close by energy, placing the atop atom on the position of the wavefunction maximum (that is, far away from the focus of the ellipse) gives a similar result that should be observed at the symmetrically opposed site. Also, a small change in the size of the ellipse shifts the eigenvalues so that the Fermi energy may tune to wavefunction number 39, that has two maxima on the principal axis of the ellipse but far away from the foci and therefore for this ellipse the mirage would not appear at the foci.

In fact, in this model there is nothing special about the foci of the ellipse. If you pick the right size and eccentricity for it so that the surface eigenfunction with energy $E_F$ has only two large symmetric maxima the splitting will also be largest. If the ellipse does not have a wavefunction at $E_f$ with such characteristics, no effect will be observed within our model. In particular, if we modify the size of the ellipse keeping the eccentricity constant, we observe alternate appearance and disappearance of wavefunctions of the described type with maxima near the foci at appropriate energies, in agreement with experiment.

This leads to the question: why ellipses? Any other corral with wavefunctions having a small number of well defined, pronounced, maxima should be as good for producing mirages. However, although we have explored several other possible shapes (ellipses narrowed at their center, for instance), ellipses seem to be the most efficient in this sense.

A final question: Is magnetism essential for obtaining a mirage? Cobalt is obviously an ideal atop atom because its local density of states develops a very narrow feature just at $E_F$: it fine-tunes itself; this is not the case for Fe, Ni, Cr, etc. However, other atoms and even non-magnetic ones may also have large densities of states near the Fermi level of the substrate, for example, S on Pd (111) As it was reported that no mirage effect appeared for S or CO on Cu(111) we decided to perform an ab-initio calculation to try to understand why this is so.

In a previous paper we calculated the electronic densities of states of a periodic system that simulates the experimental situation of an adsorbed atom on a noble metal surface. It consists of repeated slabs of five layers of Au(111) with Co atoms deposited on both sides of them forming a dilute adsorbed layer. For this purpose we used the FP-LAPW method and the LSDA approxi-
mation with the WIEN97 code [10]. The main result of that paper was that the minority spin contribution to the density of states due to the 3d orbitals of Co with \( m = 0 \) is a very narrow band precisely at \( E_F \).

In the present work we have repeated the same type of calculation for other cases, such as S and Si on Cu(111). The unit cell is the same as in the previous paper [9]; it has five noble metal layers with three atoms in each layer. One impurity atom is located on each side of the slab at one of the hollow sites of the (111) slab structure forming a \( \sqrt{3} \times \sqrt{3} \) adsorbed layer. The slabs are separated by enough empty space so as to simulate non interacting surfaces. The distance between impurity atoms on the same plane is 5 Å. As in this calculation we are intending to simulate the real material, we used the more probable position rather than the atop one.

For S on Cu(111) we found that the local density of states is not peaked at \( E_F \) but at slightly lower energies, so that if our interpretation is correct a bias voltage of 0.3 eV would help observing the mirage effect. If instead of S one would deposit Si, the tuning to the Fermi energy should be better (see Fig. 3). Because of the symmetry of the surface state, the orbitals of the adsorbed atom that should interact with it are those with \( l = 1, m = 0 \). These show a narrow feature close to \( E_F \), although not as narrow as that of Co. It must be noted that this calculation does not intend to study the interaction of the adsorbed atom with the surface state, which should not be present due to the periodic location of the adsorbed impurities, but only the interaction with the bulk noble metal that determines the position of the adsorbed atom energy with respect to the Fermi energy.

Conclusions

We have performed a calculation which gives some insight on the main features of the imaging effect of the elliptical corral and leads to suggestions for future experiments which could confirm - or not- the idea presented in this paper. It should be possible to make use of sites other than the foci of the ellipses to project atomic images. In particular, while an ellipse of \( e = 0.5 \) and \( a = 26d \) has the interesting wavefunction with its maxima near the foci (\( x = 12d \)), reducing the size to \( a = 25d \) and keeping \( e = 0.5 \) produces a wavefunction of a similar shape but with its maxima far from the foci, at \( x = 16d \) at \( E_F \). In this sense the quantum mirage appears to be quite different from classical focusing by an ellipse. Also, other atoms such as S and Si could be used, the fine tuning being achieved by proper adjustment of the voltage bias in the STM experiments.

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FIG. 1. Charge densities for the quantum corral wavefunctions number 39 to 42. The brightness indicates increasing charge density. The eigenvalues in eV are $e(39)=-5.5581$, $e(40)=-5.5578$, $e(41)=-5.5512$, $e(42)=-5.5219$. Wavefunctions 39 and 42 show two strong symmetrical maxima on the principal axis at $x=16d$ and $x=12d$ but also smaller symmetrical maxima in other places.

FIG. 2. (a) Projection of the charge density for the quantum corral wavefunction number 42 and (b),(c) corresponding split charge densities when an adsorbed atom is added at $x=12d$. The $x$ axis is the principal axis of the ellipse while the $y$ axis contains the charge density of all atoms with the same coordinate $x$.

FIG. 3. Full line: Local density of states at the adatoms S and Si adsorbed on Cu(111), close to the Fermi energy; Dotted line: Only $m=0$ states (orbital $p_z$).
Fig. 2

Charge density

a

b

c
d
Fig. 3

DOS

Energy (eV)

Si

S