Scattering Theory of Kondo Mirages and Observation of Single Kondo Atom Phase Shift

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(Received 17 August 2000)

We explain the origin of the Kondo mirage seen in recent quantum corral scanning tunneling microscope experiments with a scattering theory of electrons on the surfaces of metals. Our theory, combined with experimental data, provides a direct observation of a single Kondo atom phase shift. The Kondo mirage observed at the empty focus of an elliptical quantum corral is shown to arise from multiple electron bounces off the corral wall adatoms. We demonstrate our theory with direct quantitive comparison to experimental data.

The Kondo effect is a fascinating, many-body quantum phenomenon occurring at low temperatures, whereby a magnetic impurity in metallic bulk or on a metallic surface has its local moment screened by a cloud of conduction electrons, called the Kondo cloud, that forms in its vicinity [1]. Until recently, only bulk measurements were possible on Kondo systems, leaving isolated Kondo atoms and their scattering phase shifts unstudied. The atomic resolution of the scanning tunneling microscope (STM) now makes the study of single, isolated Kondo atoms possible [2–4]. Kondo adatoms are identified by a sharp ($\sim$10 meV wide) feature in the differential tunneling conductance (dI/dV) as a function of STM tip bias with respect to the surface of the material. The feature typically appears as a dip near the Fermi energy (E_F) in dI/dV, is localized to within $\sim$10 Å of a Kondo impurity, and is observed only at low temperatures ($\sim$4 K). If the temperature of the substrate becomes too high ($\sim$100 K), the correlations between the impurity spin and the conduction electrons are broken and the Kondo signature disappears.

Landmark STM experiments have recently discovered the remarkable fact that when a Kondo atom (Co, for example) is placed at one focus of a properly sized empty elliptical quantum corral built from Kondo adatoms, a "mirage" of the Kondo feature is cast to the opposite focus [2] more than 70 Å away. Since the Kondo effect arises from electron correlations, what does the Kondo feature at the unoccupied focus imply about local electron correlations there? An important feature of the mirage experiments is that they were done on the surface of Cu(111), which is known to have surface states that act as a two-dimensional electron gas. The central result of this Letter is to present a theory of the Kondo mirage based on electrons in this surface state scattering to infinite order from all Kondo atoms—both the Kondo atoms that make up the walls of the corral and the Kondo atom that sits at the focus. The theory is valid for all arrangements of adatoms, whether arranged in a corral shape or any other arbitrary struc-

ture including "open" structures. Electron scattering on the surface can be directly related to the dI/dV of the STM measurements. Thus, by solving the electron scattering problem on the surface in the presense of impurities we can compute the STM conductance [5].

The basic Hamiltonian in the Kondo problem is given by

$$H = \sum_{\mathbf{k}\sigma} \epsilon_k c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \frac{J}{N} \sum_{\mathbf{k},\mathbf{k}'\sigma\sigma'} \mathbf{S} \cdot \boldsymbol{\tau}_{\sigma\sigma'} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}'\sigma'}, \quad (1)$$

where ϵ_k is the dispersion relation (given by band structure calculations or experiment) of the conduction electrons, $c^\dagger_{\mathbf{k}\sigma}$ is an operator that creates an electron in the state $\mathbf{k}$ with spin σ, and $c_{\mathbf{k}\sigma}$ destroys an electron in the state $\mathbf{k}$ with spin σ. This first term describes the energy of free conduction electrons. The second term describes spin-flip scattering processes where a conduction electron flips its spin and the impurity changes its spin in response during a scattering event. N is the number of sites in the lattice, J is the coupling constant, $\mathbf{S}$ represents the impurity spin, and $\boldsymbol{\tau}_{\sigma\sigma'}$ represents the conduction electron spin. It is well known that the Kondo effect occurs when $J > 0$ [1] and the low energy properties of this Hamiltonian are described by an effective Hamiltonian with $J \rightarrow \infty$ so that the conduction electrons become "locked" into an antialigned state with the impurity moment. Spin-flip processes are thus frozen out. We do not attempt to solve this Hamiltonian but assume that we are working in the low temperature regime where spin flips are frozen out as the experiment suggests from the feature in dI/dV described in Refs. [2–4].

In the Fermi liquid description of Kondo impurities below their Kondo temperature, T_K, the impurities may be characterized by a scattering phase shift that they impart to impinging electrons (quasiparticles) [6]. For $T \ll T_K$ Kondo impurities act as potential scatterers with all the many-body physics appearing as an energy scale in the (resonant) scattering phase shift [1,6]. We apply our theory to experimental data to extract the phase shift with the

full energy dependence of a single Kondo atom, report its value, and present calculations that show beautiful *quantitative* agreement with experiment. Our theory clarifies what the STM does and does not measure in mirage experiments regarding local correlations of electrons. In particular, our theory suggests that the mirage experiments do not probe local electron-electron correlations because the Kondo correlations appear only in the theory as an energy scale, T_K, in the scattering phase shift (or alternatively, in the density of states).

We emphasize that our theory is phenomenological in that we do not attempt to compute the tunneling conductance from first principles on top of an atom as was done in [7]. Our theory is based on electron scattering which is by its nature asymptotic—an electron comes in, strikes a Kondo adatom, and leaves with a phase shift. Therefore, our theory makes accurate quantitative predictions only when the STM tip is more than 7 Å away laterally from a Kondo adatom on the surface. This is precisely the region where we can make accurate predictions about the quantum mirage with our theory. When the STM tip is within 7 Å laterally of an impurity there is accumulated screening charge and orbital density present that is not accounted for in our theory and thus the theory has no predictive power there.

When an STM tip is biased negatively with respect to the surface of a metal, such as Cu(111), electrons can tunnel from the tip onto the surface, creating a region of enhanced electron amplitude under the tip which travels outwards as a wave on the surface. Heller *et al.* [5] showed that because the Fermi wavelength of the surface state electrons on Cu(111) is much larger than the size of adatoms and because the adatoms are separated by a distance large compared to their size, it is permissible to use a multiple *s*-wave scattering expansion to calculate the electron amplitude on the surface. In this picture, the scattered electron wave and, therefore, the STM signal are determined by a single quantity: the *s*-wave phase shift of the scattered wave, $\delta_o(\epsilon)$, which will typically be complex. The imaginary part of the phase shift represents "absorption" (incoherent scattering of electrons) by the adatoms which tend to couple surface states to bulk states [5,8] resulting in a loss of electrons from the surface states.

To compute dI/dV from a scattering calculation, we follow the method of Heller *et al.* [5]. For *s*-wave scattering from a single adatom in two dimensions, the wave function is [9]

$$\psi(\mathbf{r}) \to \phi(\mathbf{r}) + f \frac{e^{i(kr - \frac{\pi}{4})}}{\sqrt{r}}, \qquad (2)$$

where the scattering amplitude, f, is $f = \frac{e^{2i\delta_o(\epsilon)} - 1}{\sqrt{2\pi k}}$. $\phi(\mathbf{r})$ is the amplitude of the circular electron wave emanating from the STM tip. There is no angular dependence of f in the *s*-wave approximation. $k = \frac{2\pi}{\lambda}$, where λ, the wavelength of the electrons on Cu(111), is 29.5 Å. $\epsilon(k) = \frac{\hbar^2 k^2}{2m^*}$ is

known from the surface state electron dispersion relation of Cu(111) which has an effective mass of $m^* = 0.38m_e$. Once $\delta_o(\epsilon)$ is determined, the surface scattering can be computed. In the limit of small bias voltages and low temperature [10],

$$\frac{dI}{dV} \propto \text{LDOS}(\vec{r}, \epsilon) = \sum_\nu |\psi_\nu(\vec{r})|^2 \delta(E_\nu - \epsilon), \qquad (3)$$

where ϵ is the energy determined by the bias voltage V and the Fermi energy E_F, via $\epsilon = E_F + eV$; ν labels the scattering eigenstates in the presence of the adatom. When several or many adatoms are present as in this paper, a multiple scattering approach [5] is used to compute $\text{LDOS}(\vec{r}, \epsilon)$. By definition the LDOS is related to the Green's function by

$$\text{LDOS}(\vec{r}, \epsilon) = -\frac{1}{\pi} \text{Im}[G_{\text{ret}}(\vec{r}, \epsilon)], \qquad (4)$$

where

$$G_{\text{ret}} = G_o + G_o T G_o \qquad (5)$$

is the retarded Green's function and T is the T matrix whose dimensions are N by N when there are N scatterers present. The T matrix contains all the information about the physical positions of the scatterers relative to each other and their corresponding phase shifts which could be different for each scatterer. $G_o(\vec{r}, \epsilon)$, is the free electron's Green's function in two dimensions. Thus, dI/dV of the STM may be obtained by solving the scattering problem.

Our theory, then, involves the following approximations, assumptions, and limitations: (i) The scattering of electrons from the adatoms is determined by a single parameter, the *s*-wave phase shift, and this must be determined from experiment or otherwise. (ii) The internal degrees of freedom (spin) of the Kondo adatoms are frozen out at the temperature of the experiment ($\sim$4 K) so we may use the results of Nozieres [6] to treat the Kondo atom as a potential scatterer with a phase shift. (iii) The adatoms are far enough apart so that we may treat the electron propagation between them as free and that RKKY interactions are sufficiently weak so that the single-impurity Kondo physics is not altered. (iv) The theory does not include any nonequilibrium effects and does not treat the charge density right at an atom correctly.

To make a direct comparison with experiment, we must obtain the phase shift of the Kondo adatoms. We do not have an *ab initio* calculation of the phase shift of a single Co adatom. Rather, we fit the resonant form of the phase shift, including inelasticity, and calculated the multiple scattering problem with this single atom data.

Since the on-atom electron orbital density is not accounted for in scattering theory, we used an on-atom fit [from experimental data of a single, isolated Co atom on Cu(111) at 4 K] involving only a renormalization of the free-space Green's function and a change in the background phase shift to compute the STM signal on top of a

Kondo adatom [7]. This on-atom fit is not part of our theory, but only a means of setting a reference point between on-atom density not accounted for in our theory and the electron density anywhere more than 7 Å away from an atom on the surface which *is* accounted for properly in our theory. This fit in no way compromises our fundamental result that the mirage is due to resonantly scattering electrons from the Kondo atoms of the walls and focus. It is used only as a method to determine as accurately as possible the phase shift of the Co on Cu(111). Determining the phase shift this way from experimental data constitutes a measurement of the single Kondo atom phase shift.

We find a good fit to the *s*-wave phase shift to be

$$\delta_o(\epsilon) = \delta_{\text{bg}} + i\delta'' + \tan^{-1}\left(\frac{\epsilon - \epsilon_o}{\Gamma/2}\right), \qquad (6)$$

where $\delta_{\text{bg}} = \frac{\pi}{4} \pm \frac{\pi}{10}$, $\delta'' = \frac{3}{2} \pm \frac{1}{4}$, $\Gamma = (9 \pm 1)$ meV, and $\epsilon_o = E_F - 1$ meV are determined by experiment. δ_{bg} is a background phase shift (possibly due to static charge screening at the impurity) that controls the resonant line shape of the adatom scattering cross section. δ'' is a measure of the inelasticity in adatom scattering and controls the attenuation of the mirage at the empty focus. $\text{Tan}^{-1}(\frac{\epsilon - \epsilon_o}{\Gamma/2})$ reflects resonant scattering due to the presence of Kondo physics. A similar form of phase shift has been derived by Újsághy *et al.* from a more microscopic point of view in [11]. The narrow spectral peak near E_F leads to resonant scattering Fermi surface electrons and sets the scale of the resonance in the phase shift. It is likely that both bulk and surface states are participating in the Kondo effect at an adatom, but the STM signal is dominated by the surface state Kondo effect in the regime of validity of our theory (>7 Å away from adatom).

Applying the theory to elliptical corrals results in the images shown in Figs. 1 and 2. The agreement with experiment is excellent. Our calculation of the tunneling spectrum at the two foci is compared with experiment in Fig. 3. Note that the signal at the unoccupied focus is attenuated by approximately a factor of 8, both experimentally and theoretically. The calculated spectroscopy in Fig. 3 most clearly demonstrates that the Kondo mirage is due only to resonant scattering of electrons from the Co adatom at the opposite focus, even though the electrons are also resonantly scattering from the wall adatoms. [Calculations performed with $\delta = i\infty$ [5] instead of $\delta_o(\epsilon)$ for the wall atoms show that the wall atoms' Kondo resonances play no essential role in the projection of the mirage to the empty focus. Experimentally the same result is found when the wall Co adatoms are replaced by CO [2].]

Only certain sized ellipses will give a good mirage effect—those which have large surface state amplitude at the foci when the scattering problem is calculated—and this depends on the relative size of the ellipse and λ_F. Only then will there be appreciable surface state electron amplitude at the focal adatom to give a Kondo effect in the sur-
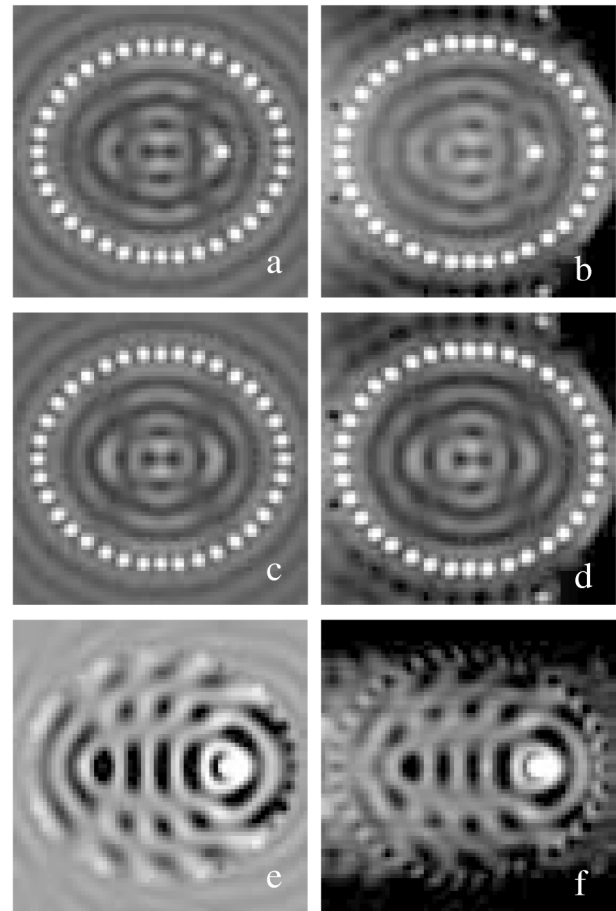

FIG. 1. Topograph standing wave patterns of a Kondo corral. Using the scattering theory and phase shifts described in the text, these STM topograph images were computed using exact Co adatom positions on Cu(111) at 4 K. The agreement between theory (*a*, *c*, and *e*) and experiment (*b*, *d*, and *f*) is remarkable. All the experimental images have been symmetrized by adding the image to itself after being reflected about its major axis. Topographic images were calculated by numerically integrating the LDOS($\vec{r}, \epsilon$) over ϵ for $E_F \leq \epsilon \leq E_F + 10$ mV. This corresponds to the topographic images taken experimentally in *b* and *d* at a bias voltage of 10 mV. *e* is the difference of *a* and *c*. *f* is the difference of *b* and *d*.

face states of Cu(111). [The relative size of surface state amplitude at a given position in the ellipse also explains why the projection of the Kondo mirage is insensitive to whether the walls are Kondo (Co) or not (CO). Near the walls, this amplitude is small in ellipses that have peaked amplitude at the foci.] Our theory predicts that the Kondo mirage is not restricted to an ellipse or even a "closed" structure. Anytime one can construct an arrangement of adatoms or other defects that lead to a buildup of surface state electron amplitude at two locations within the electron's coherence length, a mirage can be projected.

In conclusion and returning to our original question of whether the mirage reveals any information about local correlation, we conclude that it does not. There is no explicit information about electron correlations in our theory,
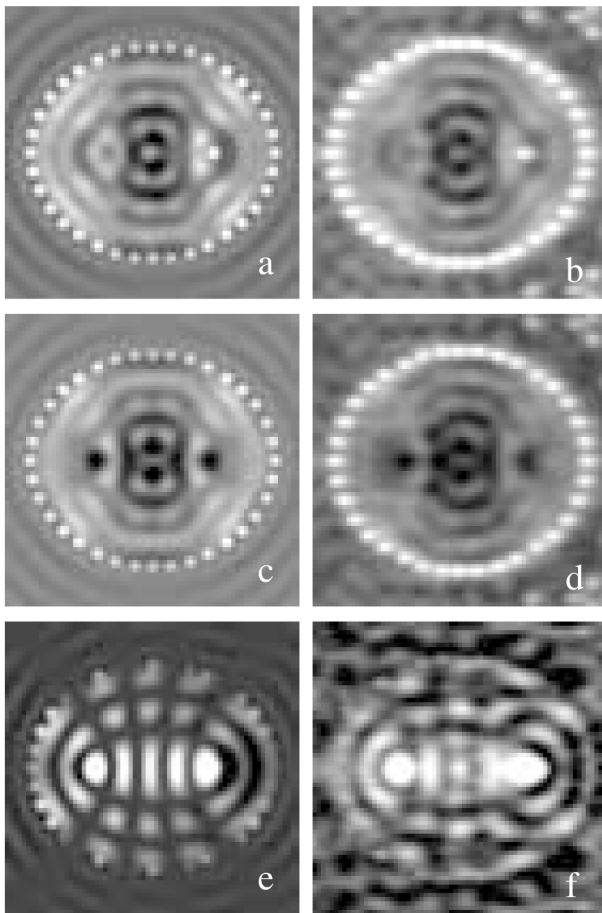
FIG. 2. dI/dV standing wave patterns of a Kondo corral. Same theory vs experiment arrangment as in Fig. 1. dI/dV measurements were taken simultaneously with topographic images at a 10 meV bias. Note that *e* and *f* resemble an eigenstate of the ellipse. The ellipse was constructed to have large surface state amplitude at the two foci.
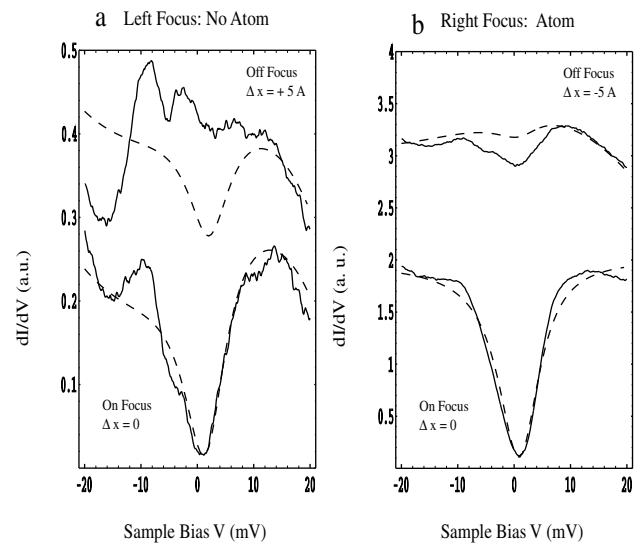

FIG. 3. Tunneling into the focal atom and empty focus: the mirage. Tunneling spectroscopy is calculated (dashed lines) with the scattering theory and phase shift given in the text at the empty focus *a*. Tunneling spectroscopy at the occupied focus is shown in *b*. A constant background slope has been removed from both the experimental data and the calculation. The attenuation of the mirage is determined by inelasticity in the scattering of electrons at the walls of the ellipse. The theoretical signal 5 Å away from the empty focus in *a* is lost in the noise of the experiment.

Note added.— While preparing this manuscript we became aware of several papers on a similar topic [12].

which gives remarkable agreement with experiment in reproducing the Kondo mirage and standing wave patterns in the elliptical corral. We are thus led to the conclusion that the mirage at the empty focus of the elliptical corral is not a result of electron correlations under the tip, but rather resonant scattering of electrons from the focal adatom and scattering (resonantly or not) from the adatoms of the walls of the corral. Intuitively this makes sense because the electrons tunneling out of the STM are unpolarized so it is not possible for the STM to give any direct information about electron correlations. The unpolarized STM returns only an average signal of spin up and spin down electrons tunneling into the surface.

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[1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, England, 1997).
[2] H. C. Manoharan, C. P. Lutz, and D. M. Eigler, Nature (London) **403**, 512 (2000).
[3] J. Li *et al.,* Phys. Rev. Lett. **80**, 2893 (1998).
[4] V. Madhavan *et al.,* Science **280**, 567 (1998).
[5] E. J. Heller *et al.,* Nature (London) **369**, 464 (1994).
[6] P. Nozieres, J. Low Temp. Phys. **17**, 31 (1974).
[7] T. Kawasaka *et al.,* J. Appl. Phys. **86**, 6970–6974 (1999); A. Schiller and S. Hershfield, Phys. Rev. B **61**, 9036 (2000).
[8] G. Hormandinger and J. B. Pendry, Phys. Rev. B **50**, 18 607 (1994); S. Crampin, M. H. Boon, and J. E. Inglesfield, Phys. Rev. Lett. **73**, 1015 (1994).
[9] L. D. Landau and E. M. Liftshitz, *Quantum Mechanics* (Butterworth-Heinemann, Oxford, 1997).
[10] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[11] O. Újsághy *et al.,* Phys. Rev. Lett. **85**, 2557 (2000).
[12] M. Weissman *et al.,* cond-mat/0007485; D. Porras *et al.,* cond-mat/0007445; O. Agam *et al.,* cond-mat/0006443.