Theory of the Fano Resonance in the STM Tunneling Density of States due to a Single Kondo Impurity

O. Újsághy,[1,2] J. Kroha,[4] L. Szunyogh,[1] and A. Zawadowski[1,2,3]

[1]*Department of Physics, Technical University of Budapest, H-1521 Budapest, Hungary*
[2]*Research Group of the Hungarian Academy of Sciences, Technical University of Budapest, H-1521 Budapest, Hungary*
[3]*Solid State and Optical Research Institute of the Hungarian Academy of Sciences, P.O.B. 49, H-1525 Budapest, Hungary*
[4]*Institut für Theorie der Kondensierten Materie, University of Karlsruhe, P.O.B. 6980, D-76128 Karlsruhe, Germany*

The conduction electron density of states nearby single magnetic impurities, as measured recently by scanning tunneling microscopy (STM), is calculated, taking into account tunneling into conduction electron states only. The Kondo effect induces a narrow Fano resonance in the conduction electron density of states. The line shape varies with the distance between STM tip and impurity, in qualitative agreement with experiments, but is very sensitive to details of the band structure. For a Co impurity the experimentally observed width and shift of the Kondo resonance are in accordance with those obtained from a combination of band structure and strongly correlated calculations.

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Recently, several groups have demonstrated using scanning tunneling microscopy [1–3] that a magnetic Kondo impurity adsorbed on the surface of a normal metal causes a narrow, resonancelike structure in the electronic surface density of states (DOS), whose asymmetric line shape resembles that of a Fano resonance [4]. The experiments were performed with single Ce atoms on Ag [1] as well as with single Co atoms on Au [2] and Cu [3] surfaces by measuring the *I-V* characteristics of the tunneling current through the tip of a scanning tunneling microscope (STM) placed close to the surface and at a small distance R from the magnetic atom [(see Fig. 1 (inset)].

Although the Kondo resonance, formed in the local conduction electron density of states (LDOS) at the Fermi energy ε_F due to resonant spin flip scattering, has been known for a long time [5], the precise line shape was not studied earlier because of the limited spatial resolution available in experiments. Wide tunnel junctions, which were proposed as measurement devices [6], probe the averaged DOS rather than the LDOS. Such experiments exhibited a giant zero bias resistance peak [7,8] or a weak conductance peak, the latter induced by assisted tunneling through impurities in the tunnel barrier [9,10].

In the present Letter we present a detailed microscopic study of the Kondo line shape as measured by STM in the vicinity of a single magnetic ion. We assume that the STM current is predominantly due to tunneling into the conduction LDOS, i.e., we neglect direct tunneling into the *d*- or *f*-level of a Co or Ce ion. This assumption is justified, because the *d*- or *f*-level is localized deeply in the atomic core. There is also direct experimental evidence for the validity of this assumption in Ref. [3], where the conduction LDOS, modified by a Kondo ion in one focus of an elliptic quantum corral, was spatially separated from the *d*-level by imaging it into the other focus, where it still did show a Fano line shape. When a discrete (single-particle) level is coupled to the conduction electron sea (bare DOS ρ_0) via a hybridization V, there is a twofold effect: (1) the discrete level is broadened and (2) the continuous conduction LDOS becomes modified. The resulting line shape in the LDOS is called Fano resonance, in reminiscence of the first study of this problem in the context of atomic physics [4]. Here we generalize this problem to the interacting case, i.e., when the discrete level arises from a many-body effect, like the Kondo resonance. It is shown that the many-body correlation effects and the consecutive Fano line shape in the conduction LDOS may be understood in separate steps, thus greatly simplifying the theoretical treatment as compared to other studies [2,11].

For concreteness we focus on a Co atom on Au and use the Anderson model [12] with a fivefold orbital degeneracy of the *d*-level $\varepsilon_d < 0$, $m = 1, \ldots, 5$,

$$H = H_0 + \varepsilon_d \sum_{m,\sigma} d^\dagger_{m,\sigma} d_{m,\sigma} + V \sum_{m\sigma\mathbf{k}} (d^\dagger_{m,\sigma} a_{\mathbf{k},\sigma} + \text{H.c.})$$
$$+ \frac{U}{2} \sum_{(m,\sigma) \neq (m',\sigma')} d^\dagger_{m,\sigma} d_{m,\sigma} d^\dagger_{m',\sigma'} d_{m',\sigma'}, \qquad (1)$$

where $H_0 = \sum_\mathbf{k} \varepsilon_\mathbf{k} a^\dagger_{\mathbf{k},\sigma} a_{\mathbf{k},\sigma}$ is the kinetic energy of the conduction electrons, and $a_{\mathbf{k},\sigma}$, $d_{m,\sigma}$ are the electron operators in the conduction band and in the *d*-level, respectively. U is the Coulomb repulsion between two electrons in any of the local levels. There are two types of resonances in the DOS of the impurity *d*-level: (i) the Co *d*-levels with a broadening $\Delta = \pi|V|^2 \rho_0$ and (ii) the Kondo resonance [13] whose width is given by the Kondo temperature T_K. In order to make contact with experiment, one must obtain realistic estimates for the parameters of the model. Therefore, we have applied the semirelativistic, screened Korringa-Kohn-Rostoker method [14] in combination with the local spin-density approximation (LSDA)

[15] for calculating the self-consistent electronic structure of a Co impurity placed onto a Au(111) surface [16]. The LSDA assumes a spontaneous magnetization and consecutive Stoner-like splitting of the local level, which is fictitious for a single impurity. Although this does not account for properties of dynamical origin like the splitting into lower and upper Hubbard states or the Kondo effect, it is an accurate method to determine static quantities like the average impurity occupation number $n_d = \sum_{m\sigma} \langle d^\dagger_{m,\sigma} d_{m,\sigma} \rangle$. This is because these are determined on time scales much shorter than the spin flip time $\tau = h/k_B T_K$, so that the local moment is effectively static for this purpose. Our LSDA results are summarized in Fig. 1: The orbital degeneracy is lifted due to crystal field splitting, and $\Delta \simeq 0.2$ eV. The on-site Coulomb repulsion U is proportional to the LSDA Stoner splitting and may be estimated as $U = 2.8$ eV [17]. Mainly due to sp-d hybridization, the Co d-levels are shifted downward compared to bulk Co, so that $n_d \simeq 8.8$ instead of $n_d = 7$ expected from the nuclear charge of Co. The excess charge is compensated by a positive conduction electron depletion cloud around the impurity. It follows that of the 11 possible charge states of the Co d-level, $z = 0, 1, \ldots, 10$, the system fluctuates only between $z = 8, 9, 10$. Using Hund's rule, these may be identified with the empty ($z = 8$, $\sigma = 1$, fixed), singly ($z = 9$, $\sigma = \pm 1/2$), and doubly ($z = 10$, $\sigma = 0$) occupied states of an effective spin-1/2 Anderson impurity model without orbital degeneracy. The level energy $\overline{\varepsilon}_d$ and Coulomb repulsion $\overline{U}$ of the effective model are different from those of the original model, Eq. (1). They may be extracted as follows [18]: According to Eq. (1) and neglecting fluctuations, the charge states $z = 0, 1, \ldots, 10$ of the d-level have energies $E(z) = z\varepsilon_d + Uz(z-1)/2$ [Fig. 2(a)]. Since $E(z)$ must have its minimum (ground state) at $z = n_d \simeq 8.8$, we have $\varepsilon_d/U = -(n_d - 1/2)$. The energies of the singly and doubly occupied orbitals, measured relative to the empty state, $E(8)$, are given

by $\overline{\varepsilon}_d = E(9) - E(8)$, $2\overline{\varepsilon}_d + \overline{U} = E(10) - E(8)$ and may be estimated as $\overline{\varepsilon}_d = -0.84$ eV, $\overline{U} = 2.84$ eV. The corresponding Co d-orbital spectral function $A_d(\omega)$, calculated using the non-crossing approximation (NCA) [19,20], is shown in Fig. 2(b). In addition to the broad peaks located near $\overline{\varepsilon}_d$ and $\overline{\varepsilon}_d + \overline{U}$ the narrow Kondo resonance is clearly seen. The Kondo temperature, $T_K = D\sqrt{2\Delta/(\pi D)} \exp\{-1/(2\rho_0 J)\}$, with the spin exchange coupling $J = \Delta/(\pi\rho_0)[1/|\overline{\varepsilon}_d| + 1/|\overline{\varepsilon}_d + \overline{U}|]$, may be estimated as $T_K \simeq 52$ K. Here D is a band cutoff provided by the bulk and (111) surface [21] bands of Au, respectively; we assume $D \simeq \varepsilon_F^{Au} = 5.5$ eV. It follows from the parabolic form of $E(z)$ [Fig. 2(a)] that $|\overline{\varepsilon}_d| < (>) \overline{\varepsilon}_d + \overline{U}_d$, if $n_d < (>) 9$. As a consequence of level repulsion, the Kondo resonance is somewhat shifted upward [present case, $n_d = 8.8$; shown in Fig. 2(c)] or downward from the Fermi level. According to local Fermi liquid theory [22], for $T < T_K$ the Kondo resonance is a pure potential scatterer. For the analytical treatment below we may, therefore, model $A_d(\omega) = \frac{1}{\pi} \mathrm{Im} G_d(\omega - i\delta)$ crudely as a sum of three Lorentzians. This corresponds to

$$G_d(\omega - i\delta) = \frac{Z_d}{\omega - \overline{\varepsilon}_d - i\Delta} + \frac{Z_U}{\omega - \overline{\varepsilon}_d - \overline{U} - i\Delta}$$
$$+ \frac{Z_K}{\omega - \varepsilon_K - iT_K}, \qquad (2)$$

where ε_K is the position of the Kondo resonance. Z_d, Z_U, and Z_K are the appropriate strengths of the poles. In the Kondo regime, at low temperatures ($T \ll T_K$), unitary scattering [22] implies $Z_K \overset{(<)}{\sim} \pi T_K/\Delta$.

We now turn to the conduction electron LDOS as measured by the STM tip at a distance R from the impurity. It is related to the electronic field operator smeared around the tip position $\mathbf{R}$ as $\Psi_{\mathbf{R},\sigma} = \int \Psi_\sigma(\mathbf{x}) U_{\mathbf{R}}(\mathbf{x}) \, d^2x$, where $U_{\mathbf{R}}(\mathbf{x})$ is a form factor centered at $\mathbf{x} = \mathbf{R}$, and $\Psi_\sigma(\mathbf{x})$ is the two-dimensional Fourier transform of $a_{\mathbf{k},\sigma}$. According

FIG. 1. LSDA result for the LDOS of a Co impurity on a Au(111) surface, showing majority ($\uparrow$) and minority ($\downarrow$) states. The inset shows the experimental setup schematically.
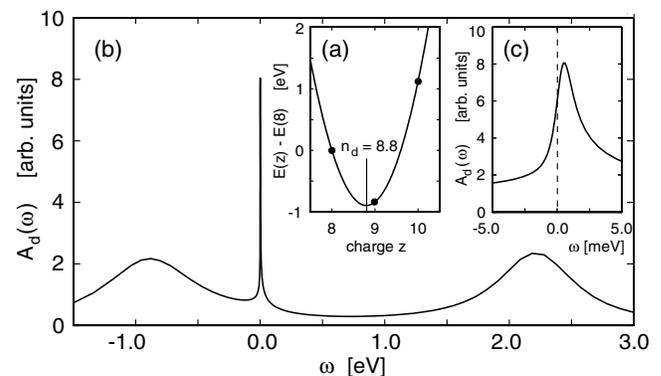
FIG. 2. (a) Energy of the relevant charge states $z = 8, 9, 10$ of the Co ion on a Au(111) surface. (b),(c) Resulting local d-orbital spectral function $A_d(\omega)$, $T = 4$ K. The broad peaks near $\overline{\varepsilon}_d$ and $\overline{\varepsilon}_d + \overline{U}$ and the shift of the Kondo resonance near ε_F are clearly visible.

to the Anderson model, the exact conduction electron t matrix is given in terms of the d-electron Green's function as $t_\sigma(i\omega_n) = \frac{\Delta}{\pi\rho_0} G_{d,\sigma}(i\omega_n)$. Then the correction to the conduction electron Green's function due to the presence of the impurity, $\delta G_{R,\sigma}(i\omega_n) = G_{R,\sigma}(i\omega_n) - G_{R,\sigma}^{(0)}(i\omega_n)$, is

$$\delta G_{R,\sigma}(i\omega_n) = G_{R,\sigma}^{(0)}(i\omega_n)\, t_\sigma(i\omega_n)\, G_{R,\sigma}^{(0)}(i\omega_n), \quad (3)$$

where $G_{R,\sigma}^{(0)}(i\omega_n) = -\langle T_\tau[\Psi_\sigma(0)\Psi_{R,\sigma}^\dagger]\rangle_{\omega_n}$. The measured perturbation in the tunneling LDOS at distance R is

$$\delta\rho_R(\omega) = \frac{1}{\pi}\,\mathrm{Im}\,\delta G_{R,\sigma}(\omega - i\delta). \quad (4)$$

Using Eq. (3), it can be expressed as

$$\delta\rho_{R,\sigma}(\omega) = \frac{1}{\pi}[\mathrm{Im}G_{R,\sigma}^{(0)}(\omega - i\delta)]^2$$
$$\times [(q_{R,\sigma}^2 - 1)\,\mathrm{Im}t_\sigma(\omega - i\delta)$$
$$+ 2\,q_{R,\sigma}\,\mathrm{Re}t_\sigma(\omega - i\delta)], \quad (5)$$

where we have defined

$$q_{R,\sigma} = \frac{\mathrm{Re}G_{R,\sigma}^{(0)}(\omega - i\delta)}{\mathrm{Im}G_{R,\sigma}^{(0)}(\omega - i\delta)}. \quad (6)$$

In the following we drop the spin index σ. $\mathrm{Im}G_R^{(0)}(\omega - i\delta)$ and q_R depend on R, but on the scale T_K very weakly on the energy; thus from here on $\omega = 0$ is taken in these quantities. At $R = 0$, $q_{R=0}$ is identical to the asymmetry parameter q of the Fano theory [4], and if $t(\omega - i\delta)$ is a simple (single-particle) level, $t(\omega - i\delta) = (\Delta/\pi\rho_0)/(\omega - \varepsilon_d - i\Delta)$, the line shape of Eq. (5) reduces to Fano's well-known expression $\rho(\omega) = \rho_0 + \delta\rho = \rho_0(x + q)^2/(x^2 + 1)$, with $x = (\omega - \varepsilon_d)/\Delta$ [4]. However, Eq. (5) is not limited to the noninteracting case. For example, in the Kondo problem, correlations are contained in $t(i\omega_n)$ and may be treated separately (see above), while the Fano line shape is due to mixing of real and imaginary parts in Eq. (5). The line shape is sensitive both to the scattering phase shift contained in $t(\omega - i\delta)$ and to the space dependent phase of the free conduction electron wave function exhibited by q_R. In particular, it depends crucially on the local charge density and on the details of the band structure [11]. In the Kondo regime ($|\overline{\varepsilon}_d|$, $\overline{U} \gg \Delta$, $T \ll T_K$), for $\omega \stackrel{<}{\sim} T_K$, $|\varepsilon_K| < T_K \ll \Delta$, and using the (approximate) unitarity relation $Z_K \stackrel{(<)}{\sim} \pi T_K/\Delta$ [see remark after Eq. (2)] the t matrix may be cast in the form

$$\mathrm{Re}t(\omega - i\delta) = \frac{1}{\rho_0}\left\{\frac{\varepsilon}{1 + \varepsilon^2} + \beta + \mathcal{O}\left(\frac{T_K}{\Delta}\right)\right\}, \quad (7a)$$

$$\mathrm{Im}t(\omega - i\delta) = \frac{1}{\rho_0}\left\{\frac{1}{1 + \varepsilon^2} - \beta\frac{\Delta}{\overline{\varepsilon}_d} + \mathcal{O}\left(\frac{T_K}{\Delta}\right)\right\}, \quad (7b)$$

where $\beta = -(Z_d/\pi)\,\overline{\varepsilon}_d\Delta/(\overline{\varepsilon}_d^2 + \Delta^2)$, and $\varepsilon = (\omega - \varepsilon_K)/T_K$. In β we have taken into account only the ninefold occupied d state, as this is closest to ε_F and the other charge states give only a small contribution to the frequency independent part of $t(\omega)$. Thus the final expression for the LDOS correction is

$$\delta\rho_R(\omega) = \frac{[\mathrm{Im}G_{R,\sigma}^{(0)}(\omega - i\delta)]^2}{\pi\rho_0}$$
$$\times \left\{\frac{2q_R\varepsilon + q_R^2 - 1}{\varepsilon^2 + 1} + C_R\right\}, \quad (8)$$

where $C_R = \beta[2q_R - (q_R^2 - 1)\Delta/\overline{\varepsilon}_d]$ arises from potential scattering by the d-level and corresponds to a weakly energy dependent Friedel oscillation. The first part coming from the scattering by the Kondo resonance gives a Fano line shape in the tunneling LDOS, controlled by the parameter q_R.

Equation (8) can be fitted to the experimental data for a Co atom on a Au(111) surface [2] with excellent agreement (Fig. 3). From the fit parameters (see the figure caption of Fig. 3) we can conclude that $\varepsilon_K > 0$. The value of the Kondo temperature $T_K \simeq 50$ K obtained from the fit is substantially smaller than the bulk value ($T_K > 300$ K for Co [13]) as the coupling of the impurity to the conduction electrons is weaker on the surface. Both T_K and the shift ε_K of the Kondo resonance are consistent with the predictions of the NCA calculation in combination with the LSDA for Co on a Au(111) surface.

The remaining task is to calculate q_R and C_R as a function of R. We have considered tunneling of electrons from the tip (1) into the three-dimensional Au bulk states as well as (2) into the two-dimensional Au(111) surface band [21]. In both cases a free electronlike band structure was assumed, neglecting, e.g., in case (2) corrections due to the herringbone surface reconstruction [21]. In case (1) the bulk Au Fermi wave number was taken as $k_F^{(b)} = 1.21$ Å^{-1}, while in case (2) it was extracted from the surface band structure mapped out in Ref. [21] by scanning tunneling spectroscopy, $k_F^{(s)} = 0.189$ Å^{-1}. A window function was adopted for the form factor $U_\mathbf{R}(\mathbf{x})$, and the scattering by the Co d orbital was taken to be isotropic, as
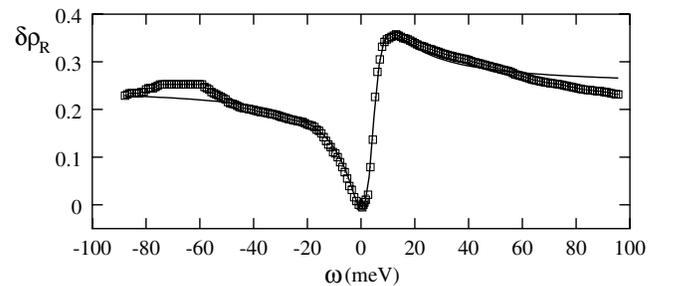
FIG. 3. Fit of Eq. (8) (solid line) to the experimental data [2] (squares) at $R = 0$. The fit parameters are $q_{R=0} = 0.66$, $C_{R=0} = 0.95$, $\varepsilon_K = 3.6$ meV, and $T_K = 5$ meV ~ 50 K.
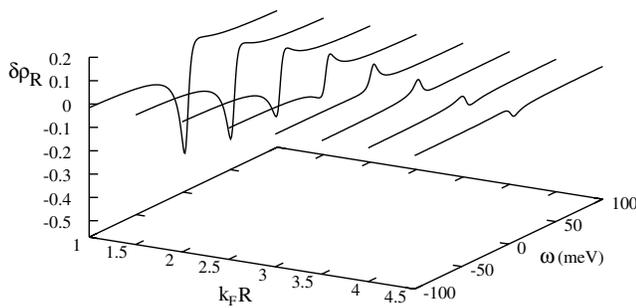
FIG. 4. Qualitative dependence of the line shape of the tunneling DOS on the distance of the tip from the impurity using the first part of Eq. (8).

the scattering phase shift does not strongly depend on angular momentum. From Eq. (8), the Lorentzian line shape with a weight $A = \mathrm{Re}[\mathcal{G}_R^{(0)}]^2/(\pi\rho_0)$ is formed at those distances R where $\mathrm{Re}\,\mathcal{G}_R^{(0)} = 0$ ($A < 0$) or $\mathrm{Im}\,\mathcal{G}_R^{(0)} = 0$ ($A > 0$). For case (1), the R dependence of the LDOS is demonstrated in Fig. 4. The line shape changes periodically between asymmetric Fano and Lorentzian line shapes, the period given by the Friedel wave length, $\lambda_F^{(b)} = \pi/k_F^{(b)} \simeq 2.6$ Å. The overall amplitude decreases with increasing distance. For case (2), the results are similar, however with an oscillation period of $\lambda_F^{(s)} = \pi/k_F^{(s)} \simeq 16.6$ Å. The latter is in good quantitative agreement with the measured [2] period of approximately 16 Å, indicating that the two-dimensional Au(111) surface band gives an important contribution to the total LDOS measured by STM. However, the precise dependence of the line shape on R is not reproduced by our simplifying assumption of a free electron band structure. In particular, the model calculation predicts an initially increasing q_R as R grows from $R = 0$, while the fit of Eq. (8) to the experiments [2] implies a decreasing q_R. The precise R dependence of q_R will require taking into account the detailed band structure as well as the additional scattering phase shift induced by the charge of the Co ion and its spatially extended screening cloud. This is beyond the scope of the present Letter.

Summarizing, we have shown that the Kondo resonance in the magnetic impurity d-level density of states ($T < T_K$) causes a Fano line shape in the density of states measured by STM even if we take into account only the tunneling into the conduction electron states. As expected, the Fano shape arises independently whether the local level is a single-particle orbital or a many-body resonance like in the Kondo effect. Superimposed on the Fano line is a weakly energy dependent Friedel oscillation induced by potential scattering off the broad d-level. From the fit to the experimental data [2] for Co on Au(111) surfaces we conclude that the Kondo resonance is shifted upward from the Fermi level, and T_K for Co on the surface is substantially reduced compared to the bulk value. By combining

electronic structure calculations (LSDA) with methods for strong correlations (NCA) these findings are reproduced semiquantitatively. In particular, the shift of the Kondo resonance is due to level repulsion between the d-level and the Kondo resonance. We demonstrated the dependence of the line shape on the distance of the tip from the impurity by using bulk as well as surface state Green's functions. We emphasize, however, that details of the band structure have to be taken into account in order to reproduce this distance dependence quantitatively.

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