Letter

Temperature evolution of the Kondo peak beyond Fermi liquid theory

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The limitation of Fermi liquid theory to very low energies and temperatures poses a fundamental problem for describing the temperature evolution of the Kondo peak. Here Fermi liquid theory for the single impurity Anderson model is extended beyond the low-energy and low-temperature regime by means of an ansatz for the impurity self-energy based on the accurate description of the Kondo peak by the Frota function, the similarity between energy and temperature in the second-order self-energy, and by exploiting Fermi liquid conditions. Analytic expressions for the temperature dependence of the Kondo peak height and width derived from this ansatz are in excellent agreement with numerical renormalization group data for temperatures beyond the Kondo temperature. The derived expression thus allows to unambiguously determine the intrinsic Kondo peak width and Kondo temperature from finite temperature measurements of the Kondo resonance.

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Scanning tunneling microscopy (STM) has become an important experimental tool for studying magnetic atoms and molecules on metallic substrates [1–13]. In these systems the coupling of the atomic or molecular spin to the conduction electrons in the substrate can give rise to the Kondo effect [14]: the magnetic moment is screened due to formation of a total spin-singlet state between the atom or molecule and the conduction electrons. The Kondo effect is signaled by the appearance of a Kondo-Fano resonance in the STM spectra [15–19]. Therefore, observation of the Kondo effect provides proof for magnetism in the uncoupled species [20,21]. Together with the possibility to detect magnetic excitations via inelastic spin tunneling [6,10,22,23], STM spectroscopy (STS) provides an excellent means for characterizing the magnetic properties of atoms, molecules, and nanoclusters.

The Kondo temperature $T_{\rm K}$ is the energy scale that controls the low-temperature dynamics of a Kondo system [24]. Importantly, $T_{\rm K}$ defines a crossover temperature at which the system enters the Kondo regime and the Kondo peak starts to emerge. In STS, $T_{\rm K}$ is conveniently determined from the halfwidth $\Gamma_{\rm K}^0$ of the Kondo peak, since $kT_{\rm K} \sim \Gamma_{\rm K}^0$ (see below for a more precise definition). However, STM spectra are often measured at temperatures comparable to $T_{\rm K}$, where the Kondo peak is strongly broadened. In order to estimate the intrinsic (i.e., zero temperature) width of the Kondo peak, the temperature evolution of the Kondo peak width is recorded and extrapolated to zero temperature. This, however, requires knowledge about the functional form of the low-temperature evolution of the Kondo peak width [25].

Using results from Fermi liquid theory (FLT) [14,26,27], Nagaoka *et al.* derived a simple expression for the temperature dependence of the Kondo peak's halfwidth [28]: $\Gamma_{\rm NA}(T) \sim \sqrt{2\,\tilde{\Delta}^2 + (\alpha kT)^2}$, where $\alpha = \pi$ [4] and $\tilde{\Delta}$ is the renormalized width in FLT (see below) related to the Kondo temperature, $kT_{\rm K} \sim \tilde{\Delta}$. This equation has been used in a number of papers to estimate the intrinsic width of the Kondo peak from finite temperature measurements [20,21,29–34]. However, in order to fit the experimental data, often the temperature coefficient α is used as an additional fit parameter, even though according to FLT α should be exactly π in the Kondo regime [14,35]. The main problem is the limitation of FLT to very low temperatures and to very low energies (or bias voltages in STS) [36,37]. For Kondo systems, temperature and energy must be well below the Kondo temperature and width, effectively one order of magnitude below $T_{\rm K}$. Especially the latter poses a fundamental problem, as it leads to a false estimate of the Kondo peak width even at zero temperature, see Fig. 1.

In order to overcome this problem, in this Letter FLT for Kondo systems will be extended to a larger range of energies and temperatures. Specifically, we focus on the single-impurity Anderson model (SIAM) [39]: a single impurity level of energy E_d subject to an on-site Coulomb repulsion U is coupled to a bath of noninteracting conduction electrons which gives rise to a constant broadening of the impurity with halfwidth Δ (wide band limit). Our starting point is the impurity Green's function (GF) for the particle-hole symmetric SIAM ($E_d = -U/2$) which according to renormalized perturbation theory (RPT) can be expressed in terms of renormalized quantities as [27]

$$G(\omega) = Z/[\omega + i\tilde{\Delta} - \tilde{\Sigma}(\omega;T)], \tag{1}$$

where the chemical potential μ has been set to zero. Z is the quasiparticle (QP) weight $Z \equiv [1 - \partial_\omega \Sigma(0;0)]^{-1}$, where $\Sigma(\omega;T)$ is the electronic self-energy resulting from the Coulomb repulsion U between electrons at the impurity site. $\tilde{\Delta} \equiv Z \cdot \Delta$ is the renormalized halfwidth of the impurity

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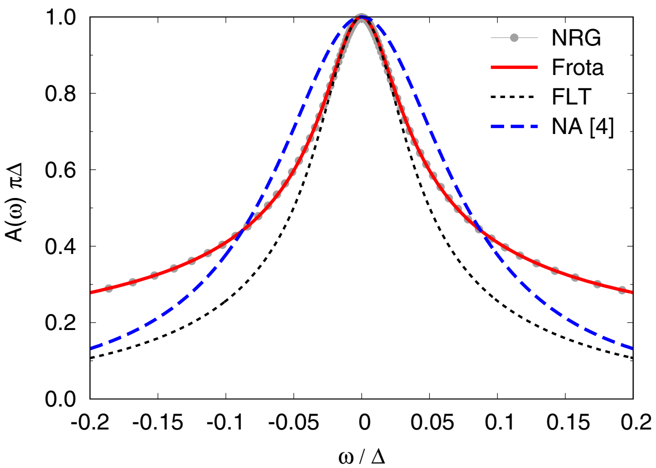

FIG. 1. SFs for the SIAM with $U = -2E_d = 10\Delta$ at $T = 0$ calculated by NRG (gray full circles) [38] compared to the approximate SFs given by FLT (black dashed line) and NA [4] (blue dashed line). Also shown is the Frota lineshape (red solid line) fitted to the NRG data with Δ_K as the fitting parameter ($\Delta_K \sim 0.0275 \cdot \Delta$) and the amplitude given by Friedel sum rule, $A_K^0 = 1/\pi\Delta$. The QP weight entering the FLT and NA expressions for the SFs is $Z \sim 0.055$, obtained from the curvature of the NRG SF at the Fermi level.

level, and $\tilde{\Sigma}(\omega;T) \equiv Z(\Sigma(\omega;T) - \Sigma(0;0) - \omega\,\partial_\omega\Sigma(0;0))$ is the renormalized self-energy, describing interaction effects between QPs. Note that at particle-hole symmetry the Hartree contribution to the self-energy $\Sigma(0,0) = U/2$ exactly cancels $E_d = -U/2$ in the denominator of the GF; also by construction, $\tilde{\Sigma}(0;0) = \partial_\omega\tilde{\Sigma}(0;0) = 0$. From the GF we can determine the spectral function (SF), $A(\omega;T) = -\text{Im}\,G(\omega;T)/\pi$, which can be directly related to the dI/dV spectra in STS [40,41].

Perturbation theory to second order [42] yields for the renormalized self-energy $\tilde{\Sigma}_2(\omega;T) = -i[\omega^2 + (\pi kT)^2]/2\tilde{\Delta}$. Hence, to second order the SF in FLT is given by $A_{\text{FLT}}(\omega;T) = -\frac{1}{\pi}\text{Im}(Z/\{\omega + i\tilde{\Delta}[1 + \frac{1}{2}(\omega/\tilde{\Delta})^2 + \frac{1}{2}(\pi kT/\tilde{\Delta})^2\})$. By making a further approximation to the FLT SF [43], Nagaoka *et al.* obtained a Lorentizan form for the SF [4], i.e., $A_{\text{NA}}(\omega;T) = \frac{1}{\pi\Delta}[(\omega/2\tilde{\Delta})^2 + 1 + (\pi kT/2\tilde{\Delta})^2]^{-1}$ with halfwidth given by $\Gamma_{\text{NA}}(T)$.

Figure 1 shows the Kondo peak in the SF computed by numerical renormalization group (NRG) [38] compared to the approximate SFs $A_{\text{FLT}}(\omega)$ and $A_{\text{NA}}(\omega)$ for $T = 0$, where the QP weight Z has been obtained by matching the curvatures of A_{FLT} at $T = 0$ and the actual Kondo peak in the NRG SF at the Fermi level, i.e., $\partial_\omega^2 A_{\text{FLT}}(0;0) = \partial_\omega^2 A(0;0)$. In FLT the halfwidth of the actual Kondo peak Γ_K^0 is considerably underestimated, even though the fit with the actual Kondo peak at low energies $\omega \ll \Gamma_K^0$ is perfect. In contrast, the Nagaoka approximation (NA) for the SF considerably overestimates the halfwidth. Additionally, the NA SF does not correctly capture the curvature of the Kondo peak at the Fermi level either. Thus, while the FLT SF yields a proper low-energy and low-temperature description of the Kondo peak, the NA actually does not.

The underestimate of the Kondo peak width in A_{FLT} is owed to the low-energy nature of FLT, limiting the validity of the SFs to energies $\omega \ll \Gamma_K^0$. The same problem arises for the temperature dependence which is likewise limited to very low temperatures $T \ll T_K \sim \Gamma_K^0$. In principle this problem could be solved by including higher order terms in the perturbation expansion. However, very high order terms would be required to achieve a meaningful extension of the energy and temperature range of FLT. But with growing order the terms also become increasingly cumbersome for an analytical treatment [44,45].

On the other hand, the Frota function $A_F(\omega) = A_K^0 \cdot \text{Re}\sqrt{i\Delta_K/(\omega + i\Delta_K)}$ [46] yields an essentially exact description of the Kondo peak for energies up to several times the halfwidth Γ_K^0, as shown by the red curve in Fig. 1. A_K^0 is the amplitude of the Frota function, while Δ_K determines its halfwidth via $\Gamma_K^0 = \sqrt{3 + \sqrt{12}} \cdot \Delta_K = 2.542 \cdot \Delta_K$. It is now important to realize that the parameters for the Frota function can be determined exactly from FLT since FLT becomes exact in the limit $\omega \to 0, T \to 0$. First, the Friedel sum rule determines the amplitude of the Kondo peak, resulting in $A_K^0 = 1/\pi\Delta$. Second, matching the curvatures of the Frota SF and FLT SF at the Fermi level, $\partial_\omega^2 A_F(0) = \partial_\omega^2 A_{\text{FLT}}(0;0)$, yields $\Delta_K = \tilde{\Delta}/2 = Z \cdot \Delta/2$. This is how Z in Fig. 1 was determined in practice; instead of taking the second derivative of the NRG spectral function numerically, which tends to be very noisy, first the Frota lineshape was determined via the Δ_K parameter, and then the QP weight via $Z = 2\Delta_K/\Delta$.

Additionally, the finding $\Delta_K = \tilde{\Delta}/2$ allows us to establish an exact relation between the Kondo temperature T_K according to Wilson [24] and the intrinsic width of the Kondo peak Γ_K^0. According to FLT $\pi\tilde{\Delta} = 4kT_K/w$, where $w = 0.4128$ is Wilson's number [14], hence $\Delta_K = 2\,kT_K/\pi w \sim 1.542\,kT_K$, and therefore,

$$\Gamma_K^0 = 2.542\,\Delta_K = \frac{2.542 \times 2}{\pi \cdot w}\,kT_K \sim 3.92\,kT_K. \qquad (2)$$

The prefactor of 3.92 is close to the value of ∼3.7 found numerically by Zitko and Pruschke from NRG calculations [47].

We next determine the renormalized self-energy $\tilde{\Sigma}$ that exactly yields the Frota lineshape at $T = 0$. First, we introduce the "Frota GF" whose imaginary part yields the Frota spectral function, $G_F(\omega) \equiv -\frac{i}{\Delta}\sqrt{i\Delta_K/(\omega + i\Delta_K)}$, where $\Delta_K = \tilde{\Delta}/2$. The corresponding renormalized self-energy that yields $G_F(\omega)$ when plugged into (1) is easily determined to be $\Sigma_F(\omega) = \omega + i2\Delta_K(1 - \sqrt{1 - i\omega/\Delta_K})$.

The crucial step now is to extend the $T = 0$ "Frota self-energy" Σ_F to finite temperatures. Inspired by the symmetry in ω and πkT of the second order contribution to the self-energy $\tilde{\Sigma}_2 \sim i[\omega^2 + (\pi kT)^2]$, we make the following Ansatz for the temperature-dependent $\tilde{\Sigma}$:

$$\tilde{\Sigma}(\omega;T) = \text{Re}\,\Sigma_F(\omega) + i\,\text{Im}\,\Sigma_F[\varepsilon(\omega;T)], \qquad (3)$$

where $\varepsilon(\omega;T) \equiv \sqrt{\omega^2 + (\pi kT)^2}$. Note that the real part of $\tilde{\Sigma}$ is crucial to recover the Frota lineshape at $T = 0$.

The real and imaginary parts of $\tilde{\Sigma}$ can be written explicitly as real functions:

$$\text{Re}\,\tilde{\Sigma}(\omega;T) = \omega - \sigma_\omega\sqrt{2}\,\Delta_K\sqrt{S(\omega/\Delta_K) - 1}, \qquad (4)$$

$$\text{Im}\,\tilde{\Sigma}(\omega;T) = 2\,\Delta_K - \sqrt{2}\,\Delta_K\sqrt{S(\varepsilon/\Delta_K) + 1}, \qquad (5)$$

where $\sigma_\omega \equiv \mathrm{sgn}(\omega)$ is the sign function and $S(x) \equiv \sqrt{1+x^2}$ has been introduced. The GF can now be written as

$$G(\omega;T) = \frac{\sqrt{2}/\Delta}{\sigma_\omega\sqrt{S\left(\frac{\omega}{\Delta_{\mathrm{K}}}\right)-1} + i\sqrt{S\left(\frac{\varepsilon(\omega,T)}{\Delta_{\mathrm{K}}}\right)+1}}. \tag{6}$$

In the limit $T \to 0$ the GF reduces to the Frota form, given by $G_{\mathrm{F}}(\omega)$. In the following we concentrate on the spectral function [48] given by the imaginary part of (6) which can be written as

$$A(\omega;T) = \frac{\sqrt{2}}{\pi\,\Delta}\frac{\sqrt{S\left(\frac{\varepsilon(\omega,T)}{\Delta_{\mathrm{K}}}\right)+1}}{S\left(\frac{\omega}{\Delta_{\mathrm{K}}}\right)+S\left(\frac{\varepsilon(\omega,T)}{\Delta_{\mathrm{K}}}\right)}. \tag{7}$$

A first test for the validity of the Ansatz (3) for the temperature dependent $\tilde{\Sigma}$ is to compute the temperature dependent height of the Kondo peak, found by evaluating A at $\omega = 0$:

$$A_0(T) = \frac{1}{\pi\,\Delta}\sqrt{\frac{2}{1+\sqrt{1+\left(\frac{\pi kT}{\Delta_{\mathrm{K}}}\right)^2}}}. \tag{8}$$

Figure 2(a) shows the height $A_0(T)$ according to (8) compared to NRG data [49], and to the height computed within FLT or NA (both approximations coincide for $\omega = 0$). The agreement between (8) and NRG is excellent for temperatures up to T_{K}, and very good for temperatures up to the bare linewidth, $kT \lesssim \Delta$. In contrast, in FLT (or NA) the decay of the SF with temperature is far too strong, leading to a severe underestimate of the Kondo peak height already for temperatures $\sim T_{\mathrm{K}}$.

Next we determine the halfwidth of the Kondo peak Γ_{K} as a function of temperature, which can be obtained from the condition $A(\Gamma_{\mathrm{K}};T) = \frac{1}{2}A_0(T)$. Inserting Eqs. (7) and (8) and squaring yields

$$S(\varepsilon/\Delta_{\mathrm{K}}) + 1 = \frac{1}{4}\frac{[S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}}) + S(\varepsilon/\Delta_{\mathrm{K}})]^2}{1+S(\pi kT/\Delta_{\mathrm{K}})}. \tag{9}$$

Using the identity $[S(\varepsilon/\Delta_{\mathrm{K}})]^2 = [S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})]^2 + (\pi kT/\Delta_{\mathrm{K}})^2$ in Eq. (9) would lead to a quartic equation for $S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})$, which could in principle be solved analytically, but leads to a very long and cumbersome expression for $S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})$. Instead we Taylor expand $S(\varepsilon/\Delta_{\mathrm{K}}) \approx S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}}) + (\pi kT/\Delta_{\mathrm{K}})^2/2S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})$, leading to $[S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}}) + S(\varepsilon/\Delta_{\mathrm{K}})]^2 \approx 4S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})^2 + 2(\pi kT/\Delta_{\mathrm{K}})^2$. This approximation leads to a biquadratic equation for $S(\Gamma_{\mathrm{K}}/\Delta_{\mathrm{K}})$ which can be solved easily. Using $\Gamma_{\mathrm{K}} = \Delta_{\mathrm{K}}\sqrt{S^2-1}$, we finally obtain the halfwidth of the Kondo peak as a function of temperature [50]:

$$\Gamma_{\mathrm{K}}(T) = \Delta_{\mathrm{K}}\cdot\sqrt{a + b\sqrt{1+\left(\frac{\pi kT}{\Delta_{\mathrm{K}}}\right)^2} + c\left(\frac{\pi kT}{\Delta_{\mathrm{K}}}\right)^2}, \tag{10}$$

where $a \equiv 1+\sqrt{3} \sim 2.732$, $b \equiv 2+\sqrt{3} \sim 3.732$, and $c \equiv \sqrt{3}/2 \sim 0.866$ are constants, and the Frota width parameter Δ_{K} yields the Kondo temperature $T_{\mathrm{K}} = \Delta_{\mathrm{K}}/1.542$ and the intrinsic halfwidth $\Gamma_{\mathrm{K}}^0 = 2.542\,\Delta_{\mathrm{K}}$.

Equation (10) is the central result of this paper. As shown in Fig. 2(b), it is in excellent agreement with NRG data for temperatures up to T_{K}, and is very accurate for temperatures up to $\Gamma_{\mathrm{K}}^0/k \sim 2.542\,\Delta_{\mathrm{K}}/k$ where it starts to deviate more strongly from NRG. In contrast, the temperature evolution of the Kondo peak width in the NA given by $\Gamma_{\mathrm{NA}}(T)$ (Eq. (8) of Ref. [4]) yields a poor description of the NRG data in the entire temperature range. The curvature in the NA in the temperature range $kT \leqslant \Delta_{\mathrm{K}}$ is very different both from the NRG data and from $\Gamma_{\mathrm{K}}(T)$ given by Eq. (10). It also leads to an overestimate of $\sim$10% for the intrinsic Kondo peak width in agreement with Fig. 1.

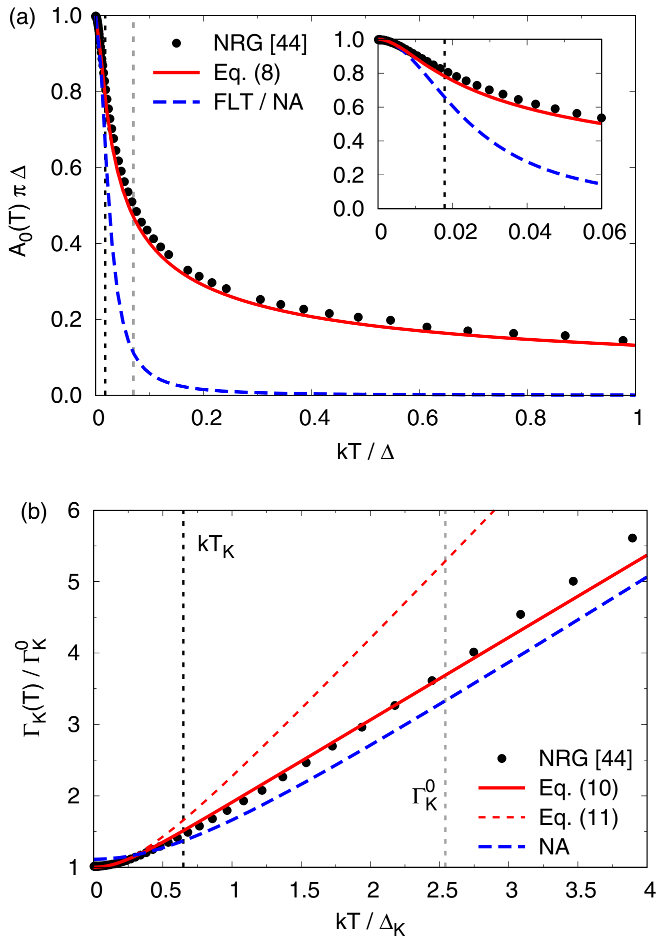

FIG. 2. Height and halfwidth of Kondo peak as functions of temperature T for the SIAM with $U = -2E_d = 10\Delta$. (a) Height $A_0(T)$ according to (8) (full red line), compared to NRG (black circles) [38,49], and to FLT/NA (dashed blue line). The inset shows a closeup of the low-temperature region. (b) Halfwidth $\Gamma_{\mathrm{K}}(T)$ according to (10) (full red line), compared to NRG (black circles) [38,49], and to the NA given by $\Gamma_{\mathrm{NA}}(T)$ (blue dashed line) [4]. The thin red dashed line shows the low-temperature approximation (11). The vertical black and gray dashed lines show $kT_{\mathrm{K}} = \Delta_{\mathrm{K}}/1.542 \sim 0.018\,\Delta$ and $\Gamma_{\mathrm{K}}^0 = 2.542\,\Delta_{\mathrm{K}} \sim 0.070\,\Delta$, respectively. The same QP weight as in Fig. 1, $Z \sim 0.055$, has been used.

A Taylor expansion of the inner square root in (10) to second order, $\sqrt{1+(\pi kT/\Delta_{\mathrm{K}})^2} \approx 1 + \frac{1}{2}(\pi kT/\Delta_{\mathrm{K}})^2$, yields an approximate expression for the halfwidth that resembles the expression found by Nagaoka *et al.* [4]:

$$\Gamma_{\mathrm{K}}(T) \approx \sqrt{\left(\Gamma_{\mathrm{K}}^0\right)^2 + (\alpha kT)^2}, \tag{11}$$

where now $\alpha = \sqrt{1+\sqrt{3}}\cdot\pi \sim 5.193$, different from π found by Nagaoka *et al.*, but also different from the values

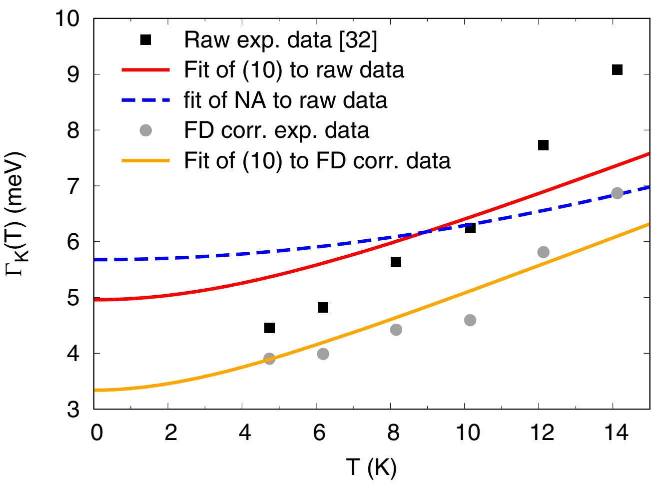

FIG. 3. Measured halfwidth of the Kondo peak versus temperature (black solid squares) and fit to $\Gamma_K(T)$ given by (10) (full red line) for the fused Goblet dimer (data from Ref. [34]), resulting in $\Delta_K \sim 1.95$ meV corresponding to $\Gamma_K^0 \sim 5.0$meV and $T_K \sim 15$ K. The blue dashed line shows a fit to the halfwidth $\Gamma_{NA}(T)$ in the NA. FD corrected halfwidths [50] are shown as solid gray circles, while the full orange line shows a fit of $\Gamma_K(T)$ given by (10) to these, resulting in $\Delta_K \sim 1.3$ meV corresponding to $\Gamma_K^0 \sim 3.3$ and $T_K \sim 9.9$ K.

found by fitting α in the NA to experimental data for spin-1/2 Kondo systems [21,31,34]. Note that Eq. (11) is only valid in the very low temperature regime $T \ll T_K$, as shown by the red dashed line in Fig. 2(b), which starts to deviate considerably from the exact result (10) for $kT \gtrsim 0.3\Delta_K \sim 0.5T_K$. However, experimental STS data is usually measured at temperatures comparable to T_K, where the approximation (11) is not accurate anymore, explaining fit values of α different from 5.193. Recently, it was also pointed out that simple square root expressions can, in general, not capture the correct behavior of Kondo linewidth both in the low and high-temperature regime [37].

Finally, we test how well Eq. (10) can be fitted to existing STS data of a spin-1/2 Kondo system. Figure 3 shows the temperature evolution of the Kondo halfwidth for the fused Goblet dimer deposited on Au(111), measured by STS [34] (black solid squares) compared to fits of the halfwidth $\Gamma_K(T)$ given by Eq. (10) (red solid line) and to $\Gamma_{NA}(T)$ in the NA (blue dashed line). While Eq. (10) performs somewhat better than the NA, it obviously does not fit very well the experimental data either, even though the temperatures are well below $\Gamma_K^0/k \sim 37$ K [34], where Eq. (10) is expected to be very accurate according to the comparison with NRG, c.f. Fig. 2(b).

A likely explanation for the disagreement is the presence of additional broadening mechanisms in the STS experiment, often not taken into account in the analysis of the STS data, as recently discussed by Gruber *et al.* [33]. For example, smearing of the Fermi-Dirac (FD) distribution at the STM tip leads to temperature-dependent broadening of the dI/dV spectra, described by a convolution of the derivative of the FD distribution and the spectral function [33,37], which can be evaluated numerically. The intrinsic halfwidth of the Kondo peak in the underlying spectral function can then be determined by numerically solving the equation for the effective halfwidth of the Kondo peak in the dI/dV [50]. The gray circles in Fig. 3 show the thus FD corrected experimental data. For the experimental temperature range the effect of FD broadening is considerable (20%–30%). As shown by the orange line in Fig. 3, the FD correction leads to a considerably better fit of Eq. (10) with the data. Importantly, it leads to a considerably lower estimate of Γ_K^0 and T_K. Also, other broadening mechanisms discussed in Ref. [33] may play a role, and further improve the fit, when taken into account. The issue of accurately measuring Kondo widths in STS experiments clearly deserves further attention.

In summary, the Fermi liquid description of the Kondo peak has been extended to a larger energy and temperature range by means of an ansatz for the temperature dependent renormalized self-energy. The extension beyond Fermi liquid theory is crucial to correctly describe the width of the Kondo peak at finite temperatures. Analytic expressions derived from this ansatz for the height and width of the Kondo peak at finite temperatures show excellent agreement with numerical renormalization group data up to experimentally relevant temperatures around T_K. The derived expression for the temperature evolution of the Kondo peak width thus allows to extract the intrinsic Kondo peak width and corresponding Kondo temperature from finite-temperature STS measurements of Kondo systems. The discrepancy with published experimental STS data of a spin-1/2 Kondo system [34] can certainly be attributed to the neglect of extrinsic broadening mechanisms in the analysis of the STS data.

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