Lecture 22: The Kondo Problem: Singlet Ground State and Kondo Resonance

In recent lectures, we have spent considerable time discussing the effect of a local magnetic moment on the electronic structure of materials. The question we turn to now it that of the ultimate fate of a local moment immersed in a sea of conduction electrons. In the large U limit, that is the limit in which the on-site repulsion energy U is much greater than the local moment resonance width Δ, we will examine the residual interaction between the local moment and the conduction electrons.

22.1 Residual Interaction Between a Local Moment and the Fermi Sea

For simplicity, we assume that the local moment has spin $S = 1/2$, as would be the case for an element such as titanium which has only one d-level available for coupling. Consider a single electron with wave vector $\vec{k}$ in a state just above the Fermi surface, and a singly occupied d-level well below the Fermi surface. If both states are occupied with the same spin, the only interesting low energy process that can happen is potential scattering of the conduction electron into a state with new momentum $\vec{k}'$.

When the states are occupied by opposite spins, virtual excitations resulting in spin exchange between the two sites are possible. The first way this for this to happen is for the conduction electron to jump into the d-level to form a doubly occupied intermediate state. This state can then decay back to the original state, or a state in which the spins are flipped relative to the original configuration. Due to the double occupation of the intermediate state, however, the system must pay the on-site repulsion cost U; the energy cost of the doubly occupied intermediate state relative to the initial configuration is $U + \epsilon_d - \epsilon_{\vec{k}}$. An alternative process through which spin exchange can take place without incurring the same-site repulsion cost is for the d-electron to be excited to a new state of momentum $\vec{k}'$, after which the excited electron of opposite spin can drop down to the now unoccupied d-level. The energy cost of this intermediate is simply $\epsilon_{\vec{k}'} - \epsilon_d$.

We can write the Hamiltonian for this interaction via the Schrieffer-Wolf transformation

$$\hat{H} = \sum_{\vec{k}\,\vec{k}'} J_{\vec{k}\,\vec{k}'} \vec{S} \cdot \vec{\mathscr{S}}_{\vec{k}'\,\vec{k}} + \sum_{\vec{k}\,\vec{k}'\,\sigma} K_{\vec{k}\vec{k}'} c^{\dagger}_{\vec{k}'\sigma} c_{\vec{k}\sigma} \tag{22.1}$$

where

$$\vec{\mathscr{S}}_{\vec{k}'\,\vec{k}} = c^{\dagger}_{\vec{k}'\alpha} \vec{\sigma}_{\alpha\beta}\, c_{\vec{k}\beta} \tag{22.2}$$

The second sum accounts for simple potential scattering of the electron outside the Fermi surface. The σ^+ and σ^- components of $\vec{\sigma}$ in the definition of $\vec{\mathscr{S}}_{\vec{k}'\,\vec{k}}$ account for the possibility of spin exchange in the Hamiltonian. For a local moment, $\vec{S} = \vec{\sigma}$. Due to the rotational invariance of spin space, the only spin operators that can appear in the Hamiltonian are the identity and scalar product $\vec{S} \cdot \vec{\mathscr{S}}_{\vec{k}'\,\vec{k}}$.

Next we must determine the coefficients $J_{\vec{k}\,\vec{k}'}$. Recall the Anderson Model, in which hybridization between the d-level and conduction band was accomplished by including the terms

$$\hat{H}_{\text{hybrid}} = \sum_{\vec{k}\,\sigma} \left\{ V_{\vec{k}}\, c^{\dagger}_{\vec{k}\sigma} c_{d\sigma} + V^{*}_{\vec{k}}\, c^{\dagger}_{d\sigma} c_{\vec{k}\sigma} \right\}$$

Thus $V_{\vec{k}}$ is the matrix element for going from the d-level to a state of momentum $\vec{k}$ above the Fermi surface, and the reverse for $V^{*}_{\vec{k}}$. Thus for the total matrix element of all exchange processes we get

$$J_{\vec{k}\,\vec{k}'} = -V_{\vec{k}} V^{*}_{\vec{k}'} \left[\frac{1}{U + \epsilon_d - \epsilon_{\vec{k}}} + \frac{1}{\epsilon_{\vec{k}'} - \epsilon_d} \right] \tag{22.3}$$

where the first term corresponds to the process with the doubly occupied intermediate, and the second corresponds to the process involving only singly occupied states.

From this point forward, all energies denoted by the symbol ε will be measured *relative to the Fermi energy*. Because we are focusing on states with momentum near the Fermi surface, $\varepsilon_{\vec{k}} \approx 0$, and hence $\varepsilon_{\vec{k}} \ll |\varepsilon_d|, U$. Thus to get an estimate of $J_{\vec{k}\,\vec{k}'}$ we can leave off the $\varepsilon_{\vec{k}}$ terms

$$J_{\vec{k}\,\vec{k}'} \approx -|V|^2 \frac{U}{|\varepsilon_d|\,(U - |\varepsilon_d|)} \tag{22.4}$$

In the strong repulsion limit,

$$U \to \infty,\ J_{\vec{k}\,\vec{k}'} \to -\frac{|V|^2}{|\varepsilon_d|}$$

Because this coupling constant is nonzero, the Hamiltonian for this system causes spin flips; as a result, the ground state is no longer simply a local moment occupied by an up-spin or a down-spin.

22.2 The Kondo Problem

We now will focus on the spin-exchange part of the Hamiltonian 22.1

$$\hat{H} = -J\vec{S} \cdot \vec{\mathscr{S}} \tag{22.5}$$

with $J > 0$. This is an *antiferromagnetic* exchange, and is sometimes referred to as "S-d exchange."

A long standing problem in solid state physics at the time of Kondo's work was the existence of a resistivity *minimum* at low but finite temperatures.[1] Based on considerations of electron-phonon scattering and impurity scattering, one would expect the resistivity to decrease with temperature down to a limiting value at $T = 0$. Observations, however, showed that below a certain temperature T_{K}, the resistivity would *increase* again, and finally saturate at a higher-than-expected value at $T = 0$.

[1] T_{K} varies drastically with host/impurity, and can be anywhere in the range 10^{-3}K to 100K.

The basic understanding of this phenomenon is that, even though one would expect the material to become "dead" as phonons freeze out as $T \to 0$, spin flips are still possible and provide a residual scattering mechanism for conduction electrons. In 1964, Kondo perturbatively calculated the scattering amplitude $t_{\vec{k}\,\vec{k}'}$ of conduction electrons by a local moment, in powers of the coupling constant J. While most of us probably would have been satisfied to stop with the first order result, Kondo continued to second order and obtained

$$t_{\vec{k}\,\vec{k}'} = J + J^2 N(0) \ln\left(\frac{\epsilon_F}{T}\right) \tag{22.6}$$

As $T \to 0$, the scattering amplitude *diverges* logarithmically in the second order term!

Resistivity R is proportional to the scattering *probability*, which is in turn proportional to $|t_{\vec{k}\,\vec{k}'}|^2$. Thus to lowest diverging order,

$$R \propto J^2 + J^3 N(0) \ln\left(\frac{\epsilon_F}{T}\right) \tag{22.7}$$

This result explains the resistivity minimum, but does not explain the observed saturation as T approaches 0. The perturbative result breaks down in this regime, but a full solution is possible using Renormalization Group methods (Wilson, *Review of Modern Physics*, 1975). The conceptual answer to the question of the fate of a local moment in a conducting Fermi sea is that a doublet state will bind to another electron to give a singlet state, leaving behind just a renormalized strength of potential scattering in the system.

22.3 Variational Approach to the Kondo Problem

Due to the breakdown of perturbation theory with the appearance of a logarithmic singularity in the electron-local moment scattering amplitude, we must seek a different approach to analyzing the Kondo S-d model.[2] The method we employ here is the variational method, starting with the trial wave function

$$|\,\psi_0\,\rangle = \left[\alpha_0 + \sum_{k<k_F,\sigma} \alpha_{\vec{k}} c^\dagger_{d\sigma} c_{\vec{k}\sigma}\right] |\,0\,\rangle \tag{22.8}$$

where $|\,0\,\rangle$ represents the filled Fermi sea ground state of the pure system.

The first term is simply the amplitude for the filled Fermi sea with the d-state empty in the trial wave function, while the second term is a superposition of states with a filled impurity d-level and a hole in the Fermi sea at momentum $\vec{k}$. In the end, the amplitude α_0 turns out to be very small, but still leaves a nonzero probability of finding the d-level empty. More interesting, however, is that this trial wave function represents a spin singlet state, while our naive expectation was to have an isolated spin filling the d-level (doublet), separate from the Fermi sea.

To calculate the variational energy of the trial wave function, we use the variational energy functional

$$\tilde{E}[|\,\psi_0\,\rangle] = \frac{\langle\,\psi_0\,|\hat{H}|\,\psi_0\,\rangle}{\langle\,\psi_0\,|\,\psi_0\,\rangle} \tag{22.9}$$

with the Hamiltonian coming from the Anderson model in the large U limit

$$\hat{H} = \varepsilon_d\, c^\dagger_d c_d + \sum_{\vec{k},\sigma} \varepsilon_{\vec{k}}\, c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma} + \sum_{\vec{k},\sigma} \left(V_{\vec{k}}\, c^\dagger_{\vec{k}} c_d + V^*_{\vec{k}}\, c^\dagger_d c_{\vec{k}}\right) + U\, n_{d\uparrow} n_{d\downarrow} \tag{22.10}$$

[2] See Phillips' book for a similar approach.

We have implicitly subtracted out the energy of the filled Fermi sea so that all energies in the Hamiltonian are measured relative to the Fermi surface. This leads to

$$\tilde{E}[|\,\psi_0\,\rangle] = \frac{2\sum_{k<k_F}\left[\alpha_{\vec{k}}^{\,2}\,(\varepsilon_d - \varepsilon_{\vec{k}}) + 2\,\alpha_0\alpha_{\vec{k}}V_{\vec{k}}\right]}{\alpha_0^{\,2} + 2\sum_{\vec{k}}\alpha_{\vec{k}}^{\,2}} \tag{22.11}$$

The 2 out front and the 2 in the denominator come from the spin sums, while the 2 in the second term of the numerator comes from the cross term. Continuing with the minimization procedure,

$$(\alpha_0^{\,2} + 2\sum_{\vec{k}}\alpha_{\vec{k}}^{\,2})\,\tilde{E} = 2\sum_{k<k_F}(\alpha_{\vec{k}}^{\,2}\,(\varepsilon_d - \varepsilon_{\vec{k}}) + 2\,\alpha_0\alpha_{\vec{k}}V_{\vec{k}}) \tag{22.12}$$

The extremum condition is $\frac{\partial\tilde{E}}{\partial\alpha_0} = \frac{\partial\tilde{E}}{\partial\alpha_{\vec{k}}} = 0$. This yields the system

$$\alpha_0\tilde{E} = 2\sum_{k<k_F}\alpha_{\vec{k}}V_{\vec{k}} \tag{22.13}$$

$$\alpha_{\vec{k}}\tilde{E} = (\varepsilon_d - \varepsilon_{\vec{k}})\,\alpha_{\vec{k}} + \alpha_0 V_{\vec{k}} \tag{22.14}$$

which can be combined through rearrangement and substitution of 22.14 in 22.13 to give the self consistent equation for $\tilde{E}$

$$\tilde{E} = 2\sum_{k<k_F}\frac{|V_{\vec{k}}|^2}{\tilde{E} - \varepsilon_d + \varepsilon_{\vec{k}}} \tag{22.15}$$

Now define the binding energy $\Delta_K = \tilde{E} - \varepsilon_d$. This quantity compares the energy of the Kondo singlet trial wave function with the energy of a singly-occupied d-level plus the filled Fermi sea (ε_d in our notation). Substituting this into the self consistent equation and using the fact that $\varepsilon_{\vec{k}} < 0$ since the only available states are those below the Fermi surface,

$$\varepsilon_d + \Delta_K = 2\sum_{k<k_F}\frac{|V_{\vec{k}}|^2}{\Delta_K + \varepsilon_{\vec{k}}} \tag{22.16}$$

$$= 2\sum_{k<k_F}\frac{|V_{\vec{k}}|^2}{\Delta_K - |\varepsilon_{\vec{k}}|} \tag{22.17}$$

If we let $V_{\vec{k}} \to V$ be a constant (independent of $\vec{k}$) and change the sum to an integral, we get

$$\varepsilon_d + \Delta_K = 2N(0)\int_0^{\epsilon_F} d\xi\,\frac{-V^2}{\xi - \Delta_K} \tag{22.18}$$

where $N(0)$ is the one-spin density of states. This is the same integral as in the BCS self consistent equation, and likewise is logarithmically divergent at low energies. This behavior comes from the existence of a sharp Fermi surface, and like in BCS theory, we always find the solution

$$\varepsilon_d + \Delta_K = -2N(0)|V|^2\ln\frac{\epsilon_F}{|\Delta_K|} \tag{22.19}$$

When the binding energy Δ_K is weak compared to the energy of the d-level relative to the Fermi surface, i.e. $\Delta_K < 0, |\Delta_K| \ll \varepsilon_d$, we can neglect Δ_K on the left hand side and rearrange to get

$$\Delta_K = -\epsilon_F e^{-\frac{1}{2N(0)V^2/\varepsilon_d}} \tag{22.20}$$

Recall that V^2/ε_d is the value we found for the coupling constant J in the S-d Hamiltonian. Thus

$$\Delta_K = -\epsilon_F e^{-\frac{1}{2N(0)J}} \tag{22.21}$$

which is *negative*. Thus the singlet ground state represented by our trial wave function is *favorable*.

The key points of our discussion up to here are summarized below:

(i) The admixture of an empty d-state into the system's wave function is important, and is needed to produce the Kondo exchange energy. This was incorporated into our model in the form of the virtual intermediate states and the Schrieffer-Wolf transformation.

(ii) With our trial wave function, the cost of having an empty d-level is reduced from $|\varepsilon_d|$ to $|\alpha_0|^2\varepsilon_d$. Thus the cost of the empty state is weighted by a small fraction, but we still gain the hybridization/hopping energy from the cross term $V\alpha_0$.

(iii) A logarithmic singularity appeared in our results because of the possibility of making hole excitations with arbitrarily low energy. That is, because of the lack of an energy gap at the Fermi surface, it is easy to excite low energy modes and to gain the hybridization energy.

We should note that we have cheated slightly in the discussion so far. We compared $\tilde{E}$ with ε_d, but the system consisting of a singly occupied d-level and a filled Fermi sea has an *odd* number of electrons. In this case we think of the spin on the d-level as pulling in one conduction electron to form a bound state; the excess spin is in a superposition of momentum states located on the Fermi surface, and thus costs no energy.

22.3.1 Kondo Temperature

The binding energy Δ_K sets an energy scale for these Kondo-type spin fluctuations. This energy scale in turn sets a temperature scale, giving us an estimate of the Kondo temperature

$$T_K \approx \Delta_K/k_B \tag{22.22}$$

Due to the exponential dependence of Δ_K on the coupling constant J, it is reasonable to expect a huge range of possible values of T_K. This is in agreement with the observation that T_K varies on the scale from 10^{-3}K to 10^2K. Note that there is no divergence of susceptibility at T_K, and that there is no actual phase transition at this temperature.

22.3.2 d-level Occupation

Because we are working in the large U (strong repulsion) limit and ε_d is large and negative, we expect the occupation $\langle n_d \rangle$ of the d-level to be close to unity. Thus we compute

$$1 - \langle n_d \rangle = \frac{{\alpha_0}^2}{{\alpha_0}^2 + 2\sum_{\vec{k}} {\alpha_{\vec{k}}}^2} \tag{22.23}$$

$$= \frac{1}{1 + 2\sum_{\vec{k}} \left(\frac{\alpha_{\vec{k}}}{\alpha_0}\right)^2} \tag{22.24}$$

Returning to the variational minimization step 22.14, we have

$$\left(\frac{\alpha_{\vec{k}}}{\alpha_0}\right)^2 = \frac{V_{\vec{k}}{}^2}{(\Delta_K + \varepsilon_{\vec{k}})^2} \tag{22.25}$$

Δ_K and $\varepsilon_{\vec{k}}$ are both less than 0, so there is no chance of division by 0.

$$2\sum_{\vec{k}} \left(\frac{\alpha_{\vec{k}}}{\alpha_0}\right)^2 = 2N(0)\int_0^{\epsilon_F} d\xi \, \frac{|V|^2}{(|\Delta_K| + |\xi|)^2} \tag{22.26}$$

$$= 2N(0)\frac{|V|^2}{\Delta_K} \tag{22.27}$$

$$= \frac{2}{\pi}\frac{\Delta}{\Delta_K} \tag{22.28}$$

where Δ is the bare resonance width of the d-level.

Thus

$$1 - \langle n_d \rangle = \frac{1}{1 + \frac{2\Delta}{\pi\Delta_K}} \tag{22.29}$$

$$\approx \frac{\pi\Delta_K}{2\Delta} \ll 1 \tag{22.30}$$

The approximation is valid because $\Delta \approx 0.5$ eV, and $\Delta_K \approx 10^-3$ eV.

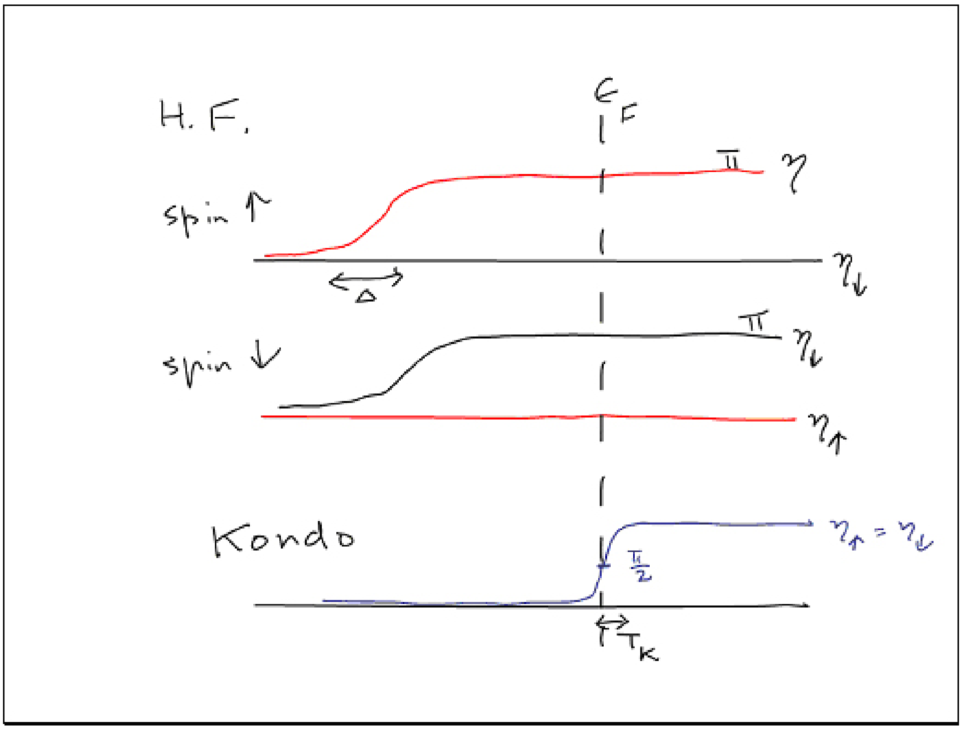
From this result we see that the deviation of the d-level occupation from unity is very small; in the variational Kondo wave function, the d-level is nearly singly occupied, but not quite. In previous lectures, we obtained the Hartree-Fock solution to the Anderson model. One key feature of this solution was that it predicted a doublet of degenerate ground states for the system. The Kondo variational ground state is a singlet, on the other hand, and does not distinguish up from down spins.

22.4 Kondo Resonance

Due to the slightly less than unit occupation of the d-level in the Kondo ground state, there is a slight excess of electron density that gets pushed up to the Fermi surface. This peak in the density of states is due to the Kondo resonance at the Fermi level, with width Δ_K and integrated area $1 - \langle n_d \rangle = \frac{\pi\Delta_K}{2\Delta}$.

The presence of this resonance at the Fermi level is more easily understood by appealing to the Friedel Sum Rule. In the simple Hartree-Fock approach, where we considered the state consisting of a singly occupied d-state plus a filled Fermi sea, we had $\langle n_{d\uparrow} \rangle = 1, \langle n_{d\downarrow} \rangle = 0$, or $\langle n_{d\uparrow} \rangle = 0, \langle n_{d\downarrow} \rangle = 1$ for the two degenerate situations. Recall from the Friedel sum rule that the phase shift η divided by π gives the total number of occupying electrons — thus for the doublet case we have $\eta_\uparrow = \pi, \eta_\downarrow = 0$ or $\eta_\uparrow = 0, \eta_\downarrow = \pi$.

In the case of the Kondo variational singlet state, since we found that the *total* occupation $\langle n_d \rangle \approx 1$, this means that $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle \approx 1/2$ (in a singlet state, the up and down spin



occupations must be the same). This means that at the Fermi energy, $\eta_{d\uparrow} = \eta_{d\downarrow} \approx \pi/2$. Thus we discover the presence of a resonance at the Fermi level (see figure).

Can we detect this resonance experimentally? One might try to use photoemission to detect the enhanced density of states near the Fermi surface, but unfortunately the resolution of this method is not good enough to resolve the feature. Other systems which exhibit behaviors characteristic of the Kondo resonance include quantum dots and scanning tunneling microscope (STM) experiments.

The quantum dot setup consists of a conducting region $100 - 1000\mathring{A}$ wide, surrounded by two conducting leads. The leads play the role of the Fermi sea, while the dot itself offers a low-lying resonant state playing the role of the impurity d-level. By applying a voltage across the leads and watching the resultant current, one can detect the presence of the resonance at ϵ_F by an increased tunneling current. For temperatures less that T_K, there is a peak in the dI/dV curve. As we know, T_K is very sensitive to the coupling constant J, which in the quantum dot setup is related to the dot-lead tunneling matrix element. This method of looking for the Kondo resonance was first proposed by Ng and Lee, and by Glazman and Raich in 1988, and observed experimentally in 1998 by Goldhaber-Gordon and Kastner.

A similar result is obtained from an STM experiment in which magnetic atoms are placed on a conducting substrate, such as cobalt on gold (Crommie, Madhaven et al. *Science*, **280**, 567.), or cerium on silver. In both experiments, however, rather than seeing a simple Lorentzian peak in dI/dV at the resonance energy, a Fano line shape is observed.

22.4.1 Fano Resonance

Why is this strange line shape observed? Consider the STM experiment with cobalt atoms adsorbed on a gold substrate. The Hamiltonian for the interaction between the STM tip denoted by subscript t, the cobalt d-level denoted by subscript d, and the conduction band of the gold substrate denoted by subscripts $\vec{k}$ is

$$\hat{H_{\text{STM}}} = T_{dt}\, c_d^\dagger c_t + T_{dt}^*\, c_t^\dagger c_d + \sum_{\vec{k}} \left[T_{\vec{k}t}\, c_{\vec{k}}^\dagger c_t + T_{\vec{k}t}^*\, c_t^\dagger c_{\vec{k}} \right] \tag{22.31}$$

This Hamiltonian reflects the possibility that electrons can tunnel from the STM tip into either the d-level of the cobalt atoms, or the conduction band of the gold substrate. Because the cobalt atoms are localized on the substrate, the tunneling amplitudes T_{dt} and $T_{\vec{k}t}$ are functions of the spatial position of the tip. Interference between these terms occurs, and is discussed in the appendix of the paper by Crommie's group (Madhaven et al. *Phys. Rev. B*, **64**, 165412.), as well as in the book by Grosso and Parravicini on page 452. The result based on these considerations is the tunneling rate

$$w \approx \text{Const.} + \frac{\left(\frac{\Delta\varepsilon}{\Gamma} + q\right)^2}{1 + \left(\frac{\Delta\varepsilon}{\Gamma}\right)^2}\, \pi \left[\sum_{\vec{k}} |T_{\vec{k}t}|^2 \delta(\varepsilon - \varepsilon_{\vec{k}}) \right] \tag{22.32}$$

with

$$\Delta\varepsilon = \varepsilon - \tilde{\varepsilon}_d \tag{22.33}$$

$$q = A/B \tag{22.34}$$

and

$$A = T_{dt} + \sum_{\vec{k}} T_{\vec{k}t} V_{d\vec{k}}\ \text{Pr}\left(\frac{1}{\varepsilon - \varepsilon_{\vec{k}}}\right) \tag{22.35}$$

$$B = \pi \sum_{\vec{k}} T_{\vec{k}t} V_{d\vec{k}}\, \delta(\varepsilon - \varepsilon_{\vec{k}}) \tag{22.36}$$

If $q \gg 1$, the tunneling is mostly into the localized d-level and a Lorentzian form is observed. For $q \to 0$, however, the tunneling current dips to zero around $\Delta\varepsilon = 0$. Why is this so? When the localized state is inserted into the system, a portion of the continuum states around the d-level are "pushed away" to make room for the new state. This results in a *depleted* continuum density of states near $\tilde{\varepsilon}_d$. Near $\tilde{\varepsilon}_d$, most of the amplitude is in the localized state, but with $q \to 0$ there is no matrix element to tunnel into this state. Thus the tunneling current dips to zero in this region.

For $q \approx 1$, a mixture of both effects is observed, thus producing the Fano line shape of a dip compounded on a peak.

22.4.2 Further Consequence of the Kondo Resonance

The electron-impurity scattering cross section is given by

$$\sigma = \frac{2}{k_F} \sum_{\ell} (\ell + 1)^2\, \sin^2(\eta_\ell - \eta_{\ell+1}) \tag{22.37}$$

If only $\ell = 2$ partial waves contribute significantly, then when $\eta_{\ell=2} = \pi/2$ the scattering cross section reaches the *unitarity limit*. That is, the scattering probability attains its maximum possible value. Thus for the singlet ground state, we see evidence for saturation of scattering probability, which in turn explains the saturation of resistivity as $T \to 0$.

In the presence of magnetic field of strength $g\mu_B H \approx k_B T_K$ it is possible to overcome the ground state's tendency towards forming a spin singlet. Above this field strength, the resistivity returns to its normal form of monotonically decreasing as $T \to 0$. In this regime where resistivity *decreases* with increasing field strength, the material exhibits a *negative* magnetoresistance.