Kondo effect in metals and nanostructures

Ramón Aguado ICMM-CSIC

Bibliography:

• P. Coleman, “Introduction to Many Body Physics” (chapters 16 and 17), Cambridge University Press, 2015

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Outline

• Historical introduction: first experimental puzzles.

• Theoretical developments that led to the understanding of the Kondo effect in metals:
  
  • the Anderson and Kondo models.
  • Kondo’s calculation.
  • Anderson’s poor’s man scaling.
  • Non-perturbative approaches.
  • Strong coupling: the Kondo resonance.

• The two-impurity Kondo problem, generalization to the lattice (slave bosons and 1/N expansions) and relevance to heavy fermion materials.
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Kondo effect in metals and nanostructures

Outline

• Modern aspects of the Kondo effect in mesoscopic systems: quantum dots and nanotubes, non-equilibrium effects, etc.

• New developments: hybrid systems (competition between superconductivity and Kondo), Shiba states, etc.

Lecture III
Breakthrough: Anderson’s scaling ideas (the art of projecting out unwanted high-energy scales)

\[ g(D') = \frac{1}{2} \frac{1}{\ln\left(\frac{D'}{T_K}\right)} \]

“The running” coupling constant

The effective coupling diverges at a dynamically generated scale: the **Kondo temperature**.

\[ T_K = D_0 \exp\left[-\frac{1}{2g_0}\right] \]
Anderson’s scaling ideas

All logarithmic corrections vanish when the high-energy cutoff equals the thermal energy:

$$g(k_B T) = \frac{1}{2} \ln \left( \frac{T}{T_K} \right)$$

• The Kondo temperature is the only scale governing the physics.
• Different systems have the same low-temperature behavior.
• All physical quantities depend on temperature only through this logarithm (universal behavior).
Origin of this saturation?

Universality: all curves fall on top of each other; details don’t matter!!
• The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson’s numerical renormalization group (Review of Modern Physics 47, 773, 1975).

• The renormalization group approach was designed for problems in which there is no characteristic energy or length scale and every energy or length makes a contribution such as critical phenomena and phase transitions. This is also the case with the Kondo problem as the integrals that lead to breakdown of perturbation theory are logarithmic.

\[
\int_{k_B T}^{D} \frac{d\varepsilon}{\varepsilon} \sim \ln\left(\frac{k_B T}{D}\right)
\]

• we cannot take the \( D \to \infty \) limit: high energy states matter.
The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson’s numerical renormalization group (Review of Modern Physics 47, 773, 1975).

To reflect this dependence, Wilson designed a logarithmic discretization of the states of the conduction band.
• The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson's numerical renormalization group (Review of Modern Physics 47, 773, 1975).

• Tight-binding chain

\[
H = J \rho \sum_{\sigma, \sigma'} S.c_0^{\dagger}_{\sigma} s_{\sigma, \sigma'} c_0_{\sigma} + \sum_{n=0}^{\infty} \sum_{\sigma} (t_n c_{n, \sigma}^{\dagger} c_{n+1, \sigma} + t_n^* c_{n+1, \sigma}^{\dagger} c_{n, \sigma})
\]

\[
t_n \approx \frac{1 + \Lambda^{-1}}{2\Lambda n/2}
\]
• The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson’s numerical renormalization group (Review of Modern Physics 47, 773, 1975).

• The low-energy part of the spectrum is obtained by iterative diagonalization adding one extra site of the chain in each step of the iterative scheme.

• The number of states would increase exponentially as new sites are added. This problem is avoided and a numerically tractable scheme is obtained if the higher lying levels are truncated in each step by keeping a fixed number of low-lying levels (typically of order $10^3$).
• The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson’s numerical renormalization group (Review of Modern Physics 47, 773, 1975).

• recurrence relation

\[ \tilde{H}_{N+1} = \Lambda^{1/2} \tilde{H}_N + \sum_{\sigma} (c_{N\sigma}^\dagger c_{N+1\sigma} + c_{N+1\sigma}^\dagger c_{N\sigma}) \]

• Many energy scales are locally coupled
The first reliable non-perturbative calculation to go well below the Kondo temperature was Wilson’s numerical renormalization group (Review of Modern Physics 47, 773, 1975).

\[ \Lambda_I = \varepsilon_d + U \]
\[ \Lambda_{II} = \varepsilon_d \]
\[ \Lambda_{III} = T_K \]

adapted from Piers Coleman, arxiv:0612006
Asymptotic freedom in condensed matter

The Kondo effect is a manifestation of the phenomenon of “asymptotic freedom” that also governs quark physics. Like the quark, at high energies the local moments inside metals are asymptotically free, but at energies below a characteristic scale, the Kondo temperature, they interact so strongly with the surrounding electrons that they become screened into a singlet state, or “confined” at low energies, ultimately forming a Landau Fermi liquid.

\[ J(\Lambda) = 0 \]
Asymptotic freedom in condensed matter

The Kondo effect is a manifestation of the phenomenon of “asymptotic freedom” that also governs quark physics. Like the quark, at high energies the local moments inside metals are asymptotically free, but at energies below a characteristic scale, the Kondo temperature, they interact so strongly with the surrounding electrons that they become screened into a singlet state, or “confined” at low energies, ultimately forming a Landau Fermi liquid.

\[ J(\Lambda) = 0 \]

\[ J(\Lambda) = \infty \]

\[ \xi_K \approx \frac{\hbar \nu_F}{k_B T_K} \]

This “Kondo cloud” is extremely long!!!
Asymptotic freedom in condensed matter

Fig. 2: (a) In isolation, the localized atomic states of an atom form a stable, sharp excitation lying below the continuum. (b) In a crystal, the $\frac{1}{2}j^2 + \frac{1}{2}$ degenerate state splits into multiplets, typically forming a low lying Kramers doublet. (c) The inverse of the Curie-Weiss susceptibility of local moments is a linear function of temperature, intersecting zero at $T_\chi$. Predicted by Philip W. Anderson [4, 5], which results from high energy valence fluctuations. Jun Kondo [6] first analyzed the effect of this scattering, showing that as the temperature is lowered, the effective strength of the interaction grows logarithmically, according to $J = J_0 + 2 J_0^2 \sim \ln(T/T_K)$ (4), where $\sim$ is the density of states of the conduction sea (per spin) and $D$ is the bandwidth. The growth of this interaction enabled Kondo to understand why in many metals at low temperatures, the resistance starts to rise as the temperature is lowered, giving rise to a resistance minimum.

Fig. 3: (a) Schematic temperature-field phase diagram of the Kondo effect. At fields and temperatures large compared with the Kondo temperature $T_K$, the local moment is unscreened with a Curie susceptibility. At temperatures and fields small compared with $T_K$, the local moment is screened, forming an elastic scattering center within a Landau Fermi liquid with a Pauli susceptibility $\sim 1/T_K$. (b) Schematic susceptibility curve for the Kondo effect, showing crossover from Curie susceptibility at high temperatures to Pauli susceptibility at temperatures below the Kondo temperature $T_K$. (c) Specific heat curve for the Kondo effect. Since the total area is the full spin entropy $R \ln 2$ and the width is of order $T_K$, the height must be of order $\sim R \ln 2 / T_K$. This sets the scale for the zero temperature specific heat coefficient. Today, we understand this logarithmic correction as a renormalization of the Kondo coupling constant, resulting from fact that as the temperature is lowered, more and more high frequency
Crossover region

\[ \chi_{\text{imp}}(T) = \frac{0.68 (g\mu_B)^2}{4k_B(T + \sqrt{2}T_K)} \]

Curie-Weiss form that corresponds to a reduced moment with respect to the free spin. Even for temperatures of the order of the Kondo temperature, the impurity moment is around 30% that of a free spin. Very slow approach to the susceptibility of a free spin.
Strong coupling

\[ \chi_{imp} (T \to 0) = \frac{0.4128 (g\mu_B)^2}{4k_B T_K} \]

FIG. 17. Plot of inverse susceptibility \( x^{-1}(T) \) vs \( T \) from the computer calculations. The magnetic moment and \( g \) factor of both the impurity and the conduction band electrons are set equal to 1. The plot actually shows \( (kT_K x)^{-1} \) vs \( T/T_K \), where \( T_K \) was defined in Eq. (IX.84). The curves represent results for two different calculations (both with \( \Lambda = 2.25 \), but \( \tilde{t} = 0.024 \) for one and 0.02412 for the other); the scatter is due to truncation errors. The zero temperature value is taken from Eq. (IX.69) and Table XVI.
Fermi liquid fixed point

Wilson was able to show that the specific heat would be a linear function of temperature, like a Fermi liquid, that could be written in a universal form.

\[ C_V = \gamma T \]

\[ \gamma = \frac{\pi^2}{3} \frac{0.4128 \pm 0.002}{8T_K} \]

\[ W = \frac{\chi/\chi^0}{\gamma/\gamma^0} = \frac{\chi}{\gamma} \left( \frac{\pi^2 k_B^2}{3 \mu_B^2} \right) = 2 \]

The Wilson ratio (the quotient between the susceptibility and the linear specific heat) is also a universal number.
For low temperatures $T$, the impurity spin is screened by the spin of conduction electrons.

The singlet consisting of the impurity spin and the screening cloud scatters other electrons.

Virtual excitations of the singlet to the triplet state lead to weak interactions between conduction electrons of opposite spin in the vicinity of the impurity.

The length scale for these interactions and for scattering from the impurity spin plus screening cloud is $\xi_K$ which is much larger than the distance between electrons.

The screening is done by electrons with energy to $\varepsilon F$.

The impurity not only causes scattering of electrons, it also induces interactions between the electrons. Since these interactions won't change on microscopic length scales, we expect that a description in terms of Fermi Liquid Theory might apply (Nozières 1975).
NRG for the Anderson model

Further confirmation of these ideas came in the form of exact results for the thermodynamics of the Kondo model by Andrei (1980) and Wiegmann (1980), by applying the Bethe Ansatz method. Later also for the Anderson model (Wiegmann, 1980).
How about **dynamics**?
How about **dynamics**?

The key quantity is the impurity spectral function

\[ \rho_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma^r(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma(\omega + i\eta) \]

\[ G_\sigma(\omega) = -i \int_{-\infty}^{\infty} dt \langle T d_\sigma(t) d_\sigma^\dagger(0) \rangle e^{i\omega t} \]
How about **dynamics**?

Physical meaning

\[ \rho_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G^r_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma(\omega + i\eta) \]

- **electron addition**
  \[ \rho_\sigma(\omega) = \sum_i |\langle i|d_\sigma^\dagger|0\rangle|^2 \delta(\omega - (E_i - E_0)) \quad \omega > 0 \]

- **electron removal**
  \[ \rho_\sigma(\omega) = \sum_i |\langle i|d_\sigma|0\rangle|^2 \delta(\omega - (E_0 - E_i)) \quad \omega < 0 \]
\[ \varepsilon_d + U \mid f_2 \rangle \]

\[ T_K \]

Kondo resonance

\[ \varepsilon_d \mid f_1 \rangle \]

\[ 2\Gamma \]
How about **dynamics**?

\[ \rho_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G^r_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma(\omega + i\eta) \]

NRG calculations: Frota & Oliveira 86, Sakai, Shimizu & Kasuya 89, Costi & Hewson 90

Abrikosov-Suhl resonance

Hubbard bands
How about **dynamics**?

NRG calculations: Frota & Oliveira 86, Sakai, Shimizu & Kasuya 89, Costi & Hewson 90)

Away from particle-hole symmetry
\[
\rho_\sigma(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma^r(\omega) = -\frac{1}{\pi} \text{Im} G_\sigma(\omega + i\eta)
\]
Adiabatic Invariant (Langreth 1966)

\[ \rho_{\sigma}(\omega) = -\frac{1}{\pi} \text{Im} G^\sigma_{\sigma}(\omega) = -\frac{1}{\pi} \text{Im} G_{\sigma}(\omega + i\eta) \]

Image Piers Coleman, Rutgers
Adiabatic Invariant (Langreth 1966)

For large U we expect the two Hubbard bands, since the spectral weight is conserved each band should contribute $1/2$.

$$\int A(\omega) d\omega = 1$$

Remarkably, the spectral function at $\omega = 0$ remains invariant as the interaction increases (always equal to the non-interacting value)

$$A(\omega = 0) = \frac{1}{\pi \Gamma} \sin^2 \delta$$

Deep result: the spectral function must always contain a peak of height $\frac{1}{\pi \Gamma} \sin^2 \delta$ and vanishingly small weight $Z \ll 1$ as U increases. This narrow resonance is a direct consequence of local Fermi liquid behaviour!

$$Z \sim \frac{T_K}{\Gamma}$$
Fermi liquid picture


Exact relations (Fermi-liquid) for the self-energy at T=0:

\[
\Sigma_\sigma(\omega \pm i\eta) = \Sigma_\sigma^R(\omega) \mp i\Sigma_\sigma^I(\omega)
\]

\[
\Sigma_\sigma^I(\varepsilon_F) = 0
\]

\[
\Sigma_\sigma^I(\omega) \propto \omega^2 \quad \omega \to \varepsilon_F
\]

\[
\text{Im} \int_{-\infty}^{\varepsilon_F} \frac{\partial \Sigma_\sigma(\omega)}{\partial \omega} G_\sigma(\omega) d\omega = 0
\]
Fermi liquid picture


Exact relations (Fermi-liquid) for the self-energy at T=0:

$$\frac{1}{\omega - \varepsilon_d + i\Gamma - \Sigma(\omega) + i\eta} = \frac{\partial}{\partial \omega} \ln(\omega - \varepsilon_d + i\Gamma - \Sigma(\omega) + i\eta) + \frac{\partial \Sigma(\omega) / \partial \omega}{\omega - \varepsilon_d + i\Gamma - \Sigma(\omega) + i\eta}$$
Fermi liquid picture


Exact relations (Fermi-liquid) for the self-energy at T=0:

\[ Im \int_{-\infty}^{\varepsilon_F} \frac{\partial \Sigma_\sigma(\omega)}{\partial \omega} G_\sigma(\omega) d\omega = 0 \]

If we integrate the density of states to get the occupation

\[ Im \int \frac{1}{\omega - \varepsilon_d + i\Gamma - \Sigma(\omega) + i\eta} = \frac{Im}{\omega - \varepsilon_d + i\Gamma - \Sigma(\omega) + i\eta} \]

\[ \langle n_\sigma \rangle = \frac{1}{2} - \frac{1}{\pi} arctan^{-1} \left( \frac{\varepsilon_d - \varepsilon_F + \Sigma_\sigma^R(\varepsilon_F) + \Sigma_\sigma^I(\varepsilon_F)}{\Gamma} \right) \]
Fermi liquid picture


Exact relations (Fermi-liquid) for the self-energy at T=0:

\[
\langle n_\sigma \rangle = \frac{1}{2} - \frac{1}{\pi} \arctan^{-1} \left( \frac{\varepsilon_d - \varepsilon_F + \Sigma^R_\sigma(\varepsilon_F)}{\Gamma} \right) = \frac{\delta_\sigma(\varepsilon_F)}{\pi}
\]

\[
\rho_\sigma(\varepsilon_F) = \frac{1}{\pi \Gamma} \sin^2 \delta_\sigma(\varepsilon_F) = \frac{1}{\pi \Gamma} \sin^2 (\pi \langle n_\sigma \rangle)
\]
The Abrikosov-Suhl resonance (or “Kondo peak”) is a direct consequence of Fermi liquid behaviour in the strong coupling limit. This physics is similar as the one giving the “coherence peaks” in Mott insulators (Leni’s lecture).
Abrikosov-Suhl resonance

Level position

\[ T_K \sim D \sqrt{\frac{2\Gamma U}{\pi}} e^{\frac{\pi\varepsilon_d (\varepsilon_d + U)}{2\Gamma U}} \]
Abrikosov-Suhl resonance

Temperature dependence

\[ t \equiv \frac{T}{T_K} \]

- - - t=43.1
- - - t=19.1
- - - t=3.78
- - - t=0.75
- - - t=0.33
- - - t=0.66
Universal behaviour (scaling) over many decades of $T$ (logarithmic) and Fermi liquid saturation is the unambiguous signature of Kondo

$$\rho(T) = n_{imp} \frac{2ne^2}{m\pi\nu(\epsilon_F)} F\left(\frac{T}{T_K}\right)$$
Heavy fermion materials

• In the periodic table, the most strongly interacting electrons reside in orbitals that are well localised.

• The properties of heavy-fermion compounds derive from the partially filled f orbitals of rare-earth or actinide ions.
Heavy fermion materials

- Heavy-fermion materials display properties which change qualitatively (unconventional superconductivity, quantum criticality, etc), depending on the temperature, so much so, that the room-temperature and low-temperature behavior almost resembles two different materials.
<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>$T^*$ (K)</th>
<th>$T_c$, $x_c$, $B_c$</th>
<th>Properties</th>
<th>$\rho$</th>
<th>$\gamma_n \text{ m J mol}^{-1} \text{K}^{-2}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>CeCu$_6$</td>
<td>10</td>
<td>–</td>
<td>Simple HF metal</td>
<td>$T^2$</td>
<td>1600</td>
<td>Stewart, Fisk and Wire (1984a) and Onuki and Komatsubara (1987)</td>
</tr>
<tr>
<td>Superconductors</td>
<td>CeCu$_2$Si$_2$</td>
<td>20</td>
<td>$T_c = 0.17$ K</td>
<td>First HFSC</td>
<td>$T^2$</td>
<td>800–1250</td>
<td>Steglich et al. (1976) and Geibel et al. (1991a,b)</td>
</tr>
<tr>
<td></td>
<td>UBe$_{13}$</td>
<td>2.5</td>
<td>$T_c = 0.86$ K</td>
<td>Incoherent metal→HFSC</td>
<td>$\rho_c \sim 800$</td>
<td>Ott, Rudigier, Fisk and Smith (1983, 1984)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CeCoIn$_5$</td>
<td>38</td>
<td>$T_c = 2.3$ K</td>
<td>Quasi 2D HFSC</td>
<td>$150 \mu\Omega \text{ cm}$</td>
<td>Petrovic et al. (2001) and Sidorov et al. (2002)</td>
<td></td>
</tr>
<tr>
<td>Kondo insulators</td>
<td>Ce$_3$Pt$_4$Bi$_3$</td>
<td>$T_X \sim 80$</td>
<td>–</td>
<td>Fully gapped KI</td>
<td>$\sim e^{\Delta/T}$</td>
<td>–</td>
<td>Hundley et al. (1990) and Bucher, Schlessinger, Canfield and Fisk (1994)</td>
</tr>
<tr>
<td></td>
<td>CeNiSn</td>
<td>$T_X \sim 20$</td>
<td>–</td>
<td>Nodal KI</td>
<td>Poor metal</td>
<td>–</td>
<td>Takabatake et al. (1990, 1992) and Izawa et al. (1999)</td>
</tr>
<tr>
<td>Quantum critical</td>
<td>CeCu$_{6-x}$Au$_x$</td>
<td>$T_0 \sim 10$</td>
<td>$x_c = 0.1$</td>
<td>Chemically tuned QCP</td>
<td>$T$</td>
<td>$\sim \frac{1}{T_0} \ln \left( \frac{T_0}{T} \right)$</td>
<td>von Löhneysen et al. (1994) and von Löhneysen (1996)</td>
</tr>
<tr>
<td></td>
<td>YbRh$_2$Si$_2$</td>
<td>$T_0 \sim 24$</td>
<td>$B_{\perp} = 0.06$ T</td>
<td>Field-tuned QCP</td>
<td>$T$</td>
<td>$\sim \frac{1}{T_0} \ln \left( \frac{T_0}{T} \right)$</td>
<td>Trovarelli et al. (2000), Paschen et al. (2004), Custers et al. (2003) and Gegenwart et al. (2005)</td>
</tr>
<tr>
<td>SC + other order</td>
<td>UPd$_2$Al$_3$</td>
<td>110</td>
<td>$T_{AF} = 14$ K, $T_{sc} = 2$ K</td>
<td>AFM + HFSC</td>
<td>$T^2$</td>
<td>210</td>
<td>Geibel et al. (1991a), Sato et al. (2001) and Tou et al. (1995)</td>
</tr>
<tr>
<td></td>
<td>URu$_2$Si$_2$</td>
<td>75</td>
<td>$T_1 = 17.5$ K, $T_{sc} = 1.3$ K</td>
<td>Hidden order and HFSC</td>
<td>$T^2$</td>
<td>120/65</td>
<td>Palstra et al. (1985) and Kim et al. (2003)</td>
</tr>
</tbody>
</table>

Unless otherwise stated, $T^*$ denotes the temperature of the maximum in resistivity. $T_c$, $x_c$, and $B_c$ denote critical temperature, doping, and field. $\rho$ denotes the temperature dependence in the normal state. $\gamma_n = C_V/T$ is the specific heat coefficient in the normal state.
Heavy fermion metals

Transport properties

• Curie-Weiss susceptibility at high T.
• Paramagnetic spin susceptibility at low T
• Quadratic temperature dependence of the low temperature resistivity.
• A dramatic enhancement of the linear specific heat.
• These transport properties suggest that Kondo physics is relevant. If this is correct, the resulting Fermi liquid at low temperatures is composed of quasiparticles with greatly enhanced masses.
Heavy fermion materials

- High temperatures: local 4f or 5f moments

\[
N = 2j + 1
\]

For example \( \text{Ce}^{3+} \)

\[
|4f^1 : j, m\rangle
\]

\[
L = 3, S = 1/2
\]

\[
J = L - S = 5/2
\]

\[
N = 6
\]

Remember, local moments have a Curie spin susceptibility

\[
\chi = \frac{(gJ\mu_B)^2 J(J + 1)}{3k_B T}
\]

\[
S = k_B \ln(2J + 1) \quad \text{Large unquenched entropy}
\]
Heavy fermion materials

The entropy can also be written as an integral of the specific heat

\[ S = k_B \ln(2J + 1) \]

\[ S = \int_{0}^{T} \frac{C_V}{T'} dT' \]

At low temperature, the Kondo effect develops and the local moments become quenched. This implies that the spin entropy is rapidly lost from the material.

This rapid loss of spin entropy forces a sudden rise in the specific heat

\[ \gamma = \lim_{T \to 0} \frac{C_V}{T} = \frac{\pi^2 k_B^2}{3} \rho^* \]

Sommerfeld coefficient

\[ \rho^* = \frac{k_F m^*}{\pi^2 \hbar^2} \]

Huge increase of effective mass at low temperatures (hence the name “Heavy Fermions”)
Heavy fermion materials

\[ \rho^* = \frac{k_F m^*}{\pi^2 \hbar^2} \]

Huge increase of effective mass at low temperatures (hence the name “Heavy Fermions”)

\[ \frac{m^*}{m_e} \sim 1000!! \]
Heavy fermion materials

Further confirmation of the Fermi-liquid behavior of heavy-fermion systems is obtained when the Sommerfeld coefficient of the linear term of the specific heat is compared with the coefficient $A$ of the resistivity:

$$\rho = \rho_0 + AT^2$$

$$\gamma \sim m^*$$

$$A \sim (m^*)^2$$

$$\frac{A}{\gamma^2} \sim \text{cons}$$

Kadowaki-Woods
Heavy fermion insulators

Transport properties

• While apparently a magnetic metal with a Curie–Weiss susceptibility at room temperature, on cooling these materials they transform continuously into a paramagnetic insulator with very tiny gaps (around 10 meV).
Development of coherence in heavy fermion systems

- Lanthanum is iso-electronic with Cerium but has an empty f-shell so the x=0 limit corresponds to a dilute Kondo system.
- As the concentration of Cerium increases, the resistivity curve starts to develop a coherence maximum and in the concentrated limit it drops to zero as a Fermi liquid.
How to explain all this?

This experimental evidence suggests that heavy fermion materials can be understood as a lattice version of the Kondo effect with a renormalised density of states.
Heavy fermion superconductors

• The early resistance to this Kondo explanation was rooted in a number of misconceptions about spin physics and the Kondo effect. Some of the first heavy-electron systems are superconductors, e.g. UBe$_{13}$, yet it was well known that small concentrations of magnetic ions, typically a few percent, suppress conventional superconductivity, so the appearance of superconductivity in a dense magnetic system appeared at first sight to be impossible!!!

• How can be explain heavy-fermion superconductors?: the Kondo effect quenches the local moments to form a new kind of heavy-fermion metal.
Heavy fermion materials

Transport properties

• High temperatures: heavy fermion compounds exhibit a large saturated resistivity, induced by incoherent spin-flip scattering of the conduction electrons of the local f moments.

• Low temperatures: Quenching of local moments (Kondo-like) together with development of phase coherence.

The simplest model which might be capable of describing heavy-fermion, mixed valence, and Kondo behavior depending on the values of the parameters is the periodic Anderson model (Varma and Yafet, Phys. Rev. B 13, 2950, 1976)

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{i,\sigma} \varepsilon_f f_{i,\sigma}^\dagger f_{i,\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \\
\sum_{i,k,\sigma} (V_k e^{-ik \cdot R_i} c_{k,\sigma}^\dagger f_{i,\sigma} + V_k^* e^{ik \cdot R_i} f_{i,\sigma}^\dagger c_{k,\sigma})
\]
\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{i,\sigma} \varepsilon_f f_{i,\sigma}^\dagger f_{i,\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \\
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\]

**Non-interacting case**

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \varepsilon_f f_{k,\sigma}^\dagger f_{k,\sigma} + \\
\sum_{k,\sigma} (V_k c_{k,\sigma}^\dagger f_{k,\sigma} + V_k^* f_{k,\sigma}^\dagger c_{k,\sigma})
\]

Bloch representation
\begin{align*}
H &= \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{i,\sigma} \epsilon_f f_{i,\sigma}^\dagger f_{i,\sigma} + \sum_{i} U n_{i\uparrow} n_{i\downarrow} + \\
&\quad \sum_{i,k,\sigma} (V_k e^{-ik.R_i} c_{k,\sigma}^\dagger f_{i,\sigma} + V_k^* e^{ik.R_i} f_{i,\sigma}^\dagger c_{k,\sigma})
\end{align*}

Non-interacting case

\begin{align*}
H &= \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \epsilon_f f_{k,\sigma}^\dagger f_{k,\sigma} + \\
&\quad \sum_{k,\sigma} (V_k c_{k,\sigma}^\dagger f_{k,\sigma} + V_k^* f_{k,\sigma}^\dagger c_{k,\sigma})
\end{align*}

Bloch representation

\begin{align*}
\alpha_{k,\sigma}^{(+)} &= u_k c_{k,\sigma} + v_k f_{k,\sigma} \\
|u_k|^2 &= \frac{1}{2} [1 + \frac{\epsilon_k - \epsilon_f}{\sqrt{(\epsilon_k - \epsilon_f)^2 + 4|V_k|^2}}]
\end{align*}

\begin{align*}
\alpha_{k,\sigma}^{(-)} &= -v_k c_{k,\sigma} + u_k f_{k,\sigma} \\
|v_k|^2 &= \frac{1}{2} [1 - \frac{\epsilon_k - \epsilon_f}{\sqrt{(\epsilon_k - \epsilon_f)^2 + 4|V_k|^2}}]
\end{align*}

\begin{align*}
E_k^\pm &= \frac{1}{2} (\epsilon_k + \epsilon_f \pm \sqrt{(\epsilon_k - \epsilon_f)^2 + 4|V_k|^2})
\end{align*}
\[ H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \varepsilon_f f_{k,\sigma}^\dagger f_{k,\sigma} + \sum_{k,\sigma} (V_k c_{k,\sigma}^\dagger f_{k,\sigma} + V_k^* f_{k,\sigma}^\dagger c_{k,\sigma}) \]

\[ E_{k}^{\pm} = \frac{1}{2} (\varepsilon_k + \varepsilon_f \pm \sqrt{(\varepsilon_k - \varepsilon_f)^2 + 4|V_k|^2}) \]

Non-interacting hybridization gap
The relevant question is how interactions renormalize these bands and, in particular, how to obtain a minigap of the order of $T_K$ characteristic of heavy fermion “Kondo insulators”

$$H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \varepsilon_f f_{k,\sigma}^\dagger f_{k,\sigma} + \sum_{k,\sigma} (V_k c_{k,\sigma}^\dagger f_{k,\sigma} + V_k^* f_{k,\sigma}^\dagger c_{k,\sigma})$$

$$H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \tilde{\varepsilon}_f f_{k,\sigma}^\dagger f_{k,\sigma} + \sum_{k,\sigma} (\tilde{V}_k c_{k,\sigma}^\dagger f_{k,\sigma} + \tilde{V}_k^* f_{k,\sigma}^\dagger c_{k,\sigma})$$
Doniach’s Kondo lattice

Simpler than Anderson, Doniach just considered spins on a lattice

\[ H = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + J \sum_j \sum_{\alpha \beta} \vec{S}_j \cdot \vec{c}_{k\alpha}^\dagger \vec{\sigma}_{\alpha \beta} c_{k' \beta} e^{i(k' - k) \cdot R_j} \]

Most local moments develop an antiferromagnetic order at low temperatures. A magnetic moment at a given location induces a wave of Friedel oscillations in the electron spin density (RKKY interaction, Mª José Calderón’s lectures)

\[ \langle \vec{\sigma}(x) \rangle = -J \chi(x - x_0) \langle \vec{S}(x_0) \rangle \]

\[ \chi(x - x_0) = 2 \sum_{k,k'} \left( \frac{f(\varepsilon_k) - f(\varepsilon_{k'})}{\varepsilon_{k'} - \varepsilon_k} \right) e^{i(k - k')x} \]

Non-local susceptibility
Doniach’s Kondo lattice

\[ \langle \vec{\sigma}(x) \rangle = -J \chi(x - x_0) \langle \vec{S}(x_0) \rangle \]

\[ \langle \vec{\sigma}(r) \rangle \sim -J \rho \frac{\cos 2k_F r}{|k_F r|^3} \]

\[ H_{RKKY} \sim -J^2 \chi(x - x_0) \vec{S}(x) . \vec{S}(x_0) \]
Doniach’s Kondo lattice

\[ H_{RKKY} \sim -J^2 \chi(x-x_0)\bar{\sigma}(x)\bar{\sigma}(x_0) \]

Competition of two energy scales

\[ T_K \sim D \exp[-1/J\rho] \]

\[ T_N \sim J^2 \rho \]

AFM

Fermi Liquid

\[ T_K < T_{RKKY} \]

\[ T_K > T_{RKKY} \]
Doniach’s Kondo lattice

Competition of two energy scales

Minimal realization where this competition already appears: the two-impurity Kondo problem, the ground state changes from Kondo singlet to AF singlet when

\[ \frac{J}{T_K} \sim 2 \]

How to treat lattices beyond this phenomenological picture? A powerful technique to capture the strong coupling limit is the large N approach.
The relevant question is how interactions renormalize these bands and, in particular, how to obtain a minigap of the order of $T_K$ characteristic of heavy fermion “Kondo insulators”

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^{\dagger} c_{k,\sigma} + \sum_{k,\sigma} \varepsilon_f f_{k,\sigma}^{\dagger} f_{k,\sigma} + \\
\sum_{k,\sigma} (V_k c_{k,\sigma}^{\dagger} f_{k,\sigma} + V_k^{*} f_{k,\sigma}^{\dagger} c_{k,\sigma})
\]

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^{\dagger} c_{k,\sigma} + \sum_{k,\sigma} \tilde{\varepsilon}_f f_{k,\sigma}^{\dagger} f_{k,\sigma} + \\
\sum_{k,\sigma} (\tilde{V}_k c_{k,\sigma}^{\dagger} f_{k,\sigma} + \tilde{V}_k^{*} f_{k,\sigma}^{\dagger} c_{k,\sigma})
\]
\[ H = \sum_{k,\sigma} \varepsilon_k c^\dagger_{k,\sigma} c_{k,\sigma} + \sum_{i,\sigma} \varepsilon_f f^\dagger_{i,\sigma} f_{i,\sigma} + \sum_i U n_{i\uparrow} n_{i\downarrow} + \sum_{i,k,\sigma} (V_k e^{-ik\cdot R_i} c^\dagger_{k,\sigma} f_{i,\sigma} + V_k^* e^{ik\cdot R_i} f^\dagger_{i,\sigma} c_{k,\sigma}) \]

Narrow f-bands, such as Cerium, the ratio \( U \) to the band width is extremely large:

\[ U \to \infty \]

Double occupancy of the orbitals becomes forbidden.
Double occupancy of the orbitals becomes forbidden

\[ H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f |1, \sigma \rangle \langle 1, \sigma | + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger |0, 0 \rangle \langle 1, \sigma | + V_k^* |1, \sigma \rangle \langle 0, 0 | c_{k,\sigma} \]

On each site

\[ X_{pq} = |p\rangle \langle q| \]

are Hubbard operators that restrict the Hilbert space to the desired physical sector; such constraint is just given by the completeness relation

\[ \sum_q X_{qq} = |q\rangle \langle q| = 1 \]

Note: these many-body operators do not follow standard commutation/anticommutation rules

\[ |q\rangle \langle p| |p'\rangle \langle q'| = \delta_{p,p'} |q\rangle \langle q'| \]

Similar to spin operators, Wicks theorem is not valid and standard perturbation theory cannot be applied.
Double occupancy of the orbitals becomes forbidden

\[ H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f |1, \sigma\rangle \langle 1, \sigma| + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger |0, 0\rangle \langle 1, \sigma| + V_k^* |1, \sigma\rangle \langle 0, 0| c_{k,\sigma} \]

On each site

\[ f_\sigma \rightarrow |0, 0\rangle \langle 1, \sigma| \quad f_\sigma^\dagger \rightarrow |1, \sigma\rangle \langle 0, 0| \]

\[ X_{pq} = |p\rangle \langle q| \]

\[ \sum_q X_{qq} = |q\rangle \langle q| = 1 \quad \rightarrow \quad \sum_\sigma f_\sigma^\dagger f_\sigma + |0, 0\rangle \langle 0, 0| = 1 \]

Trick: replace physical fermion by slave boson and fermion (exact). Physically these degrees of freedom represent charge fluctuations and spin fluctuations, respectively.

\[ f_\sigma^\dagger \rightarrow d_\sigma^\dagger b \]
Double occupancy of the orbitals becomes forbidden

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f |1, \sigma\rangle \langle 1, \sigma| + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger |0, 0\rangle \langle 1, \sigma| + V_k^* |1, \sigma\rangle \langle 0, 0| c_{k,\sigma}
\]

\[
H = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger d_{\sigma} b^\dagger + V_k^* d_{\sigma}^\dagger c_{k,\sigma} b
\]

Provided that we work with the constraint

\[
\sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} + b^\dagger b = 1
\]

Double occupancy of the orbitals becomes forbidden

Work with generalized Hamiltonian, includes Lagrange multiplier to take care of constraint

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger d_{\sigma} b^\dagger + V_k^* d_{\sigma}^\dagger c_{k,\sigma} b + \lambda (b^\dagger b + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1)
\]
Double occupancy of the orbitals becomes forbidden

\[ U \rightarrow \infty \]

Work with generalized Hamiltonian, includes Lagrange multiplier to take care of constraint

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger d_{\sigma} b^\dagger + V_k^* d_{\sigma}^\dagger c_{k,\sigma} b + \lambda (b^\dagger b + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1)
\]

Remember: f local moments have large degeneracies

Low lying magnetic multiplet

\[
N = 2j + 1
\]
Double occupancy of the orbitals becomes forbidden

\[ H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \sum_{k,\sigma} V_k c_{k,\sigma}^\dagger d_{\sigma} b_{\sigma}^\dagger + V_k^* d_{\sigma}^\dagger c_{k,\sigma} b + \lambda (b^\dagger b + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1) \]

• One can perform controlled \( \frac{1}{N} \) expansions

• The “mean field” limit \( N \to \infty \) gives the strong coupling limit we seek!
Large N

\[ H_I(j) = \frac{J}{N} S_{\alpha\beta}(j) c_{j\alpha}^{\dagger} c_{j\beta} = -\frac{J}{N} (c_{j\beta}^{\dagger} f_{j\beta})(f_{j\alpha}^{\dagger} c_{j\alpha}) \]

This kind of interaction can be factorized using Hubbard-Stratonovich:

\[ -g A^{\dagger} A \rightarrow A^{\dagger} V + \bar{V} A + \frac{\bar{V} V}{g} \]

\[ H_I(j) \rightarrow \bar{V}_j (c_{j\beta}^{\dagger} f_{j\beta}) + (f_{j\alpha}^{\dagger} c_{j\alpha}) V_j + N \frac{\bar{V}_j V_j}{J} \]

Exact provided that the auxiliary V are treated as quantum fluctuating fields. As we have seen, these fields have a physical meaning in the context of the Anderson model ("slave bosons" that govern valence fluctuations).
Large $N$

$$H_I(j) \rightarrow \bar{V}_j (c_{j\beta}^\dagger f_{j\beta}) + (f_{j\alpha}^\dagger c_{j\alpha})V_j + N \frac{\bar{V}_j V_j}{J}$$

Exact provided that the auxiliary $V$ are treated as quantum fluctuating fields. As we have seen, these fields have a physical meaning in the context of the Anderson model ("slave bosons" that govern valence fluctuations).
Large N

• Very powerful method as it allows systematic expansion in $\frac{1}{N}$

Kadanoff-Baym generating function

Non-crossing approximation (NCA)

Pseudo-fermion selfenergy

$\frac{1}{\sqrt{N}}$ $\frac{1}{\sqrt{N}}$

$O(\frac{1}{N})$

Slave boson selfenergy

$\sum_{\sigma=1}^{N} \frac{1}{\sqrt{N}}$

$O(1)$
Large N

- Very powerful method as it allows systematic expansion in $\frac{1}{N}$
- Non-perturbative self-consistent expansion.

- It can be generalized to non-equilibrium using Keldysh Green’s functions techniques. As we will see, very useful for Kondo transport in nanostructures

$\mathbf{U} \rightarrow \infty$

Double occupancy of the orbitals becomes forbidden

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \frac{V_0}{\sqrt{N}} \sum_{k,\sigma} (c_{k,\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{k,\sigma} + b^\dagger b + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1)
\]

Mean field

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \frac{V_0 \langle b \rangle}{\sqrt{N}} \sum_{k,\sigma} (c_{k,\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{k,\sigma}) + \lambda(\langle b \rangle^2 + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1)
\]

Renormalized parameters

\[
\tilde{V} = \frac{V_0 \langle b \rangle}{\sqrt{N}} = V_0 \tilde{b} \quad \tilde{\varepsilon}_f = \varepsilon_f + \lambda
\]
$U \rightarrow \infty$

Double occupancy of the orbitals becomes forbidden

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \frac{V_0 \langle b \rangle}{\sqrt{N}} \sum_{k,\sigma} (c_{k,\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{k,\sigma}) + \lambda (\langle b \rangle^2 + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1)
\]

Effective non-interacting resonant level model with renormalized parameters!!

\[
\tilde{V} = \frac{V_0 \langle b \rangle}{\sqrt{N}} = V_0 \tilde{b} \quad \tilde{\varepsilon}_f = \varepsilon_f + \lambda
\]
\[ U \rightarrow \infty \]

Double occupancy of the orbitals becomes forbidden

\[
H(\lambda) = \sum_{k,\sigma} \varepsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{\sigma} \varepsilon_f d_{\sigma}^\dagger d_{\sigma} + \frac{V_0\langle b \rangle}{\sqrt{N}} \sum_{k,\sigma} (c_{k,\sigma}^\dagger d_{\sigma} + d_{\sigma}^\dagger c_{k,\sigma}) + \lambda \langle \langle b \rangle \rangle^2 + \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma} - 1
\]

Solution: solve the selfconsistent set of equations

\[
\tilde{b}^2 + \frac{1}{N} \sum_{\sigma} \langle d_{\sigma}^\dagger d_{\sigma} \rangle = \frac{1}{N}
\]

\[
\frac{\tilde{V}}{N} \sum_{k,\sigma} \langle c_{k,\sigma}^\dagger d_{\sigma} \rangle + (\tilde{\varepsilon}_f - \varepsilon_f) \tilde{b}^2 = 0
\]
$U \to \infty$

Double occupancy of the orbitals becomes forbidden

$$\tilde{\Gamma} = \pi \tilde{V}^2 \nu(\varepsilon_F) = \tilde{b}^2 \Gamma$$

$$\rho(\varepsilon) = \frac{1}{\pi} \frac{\tilde{\Gamma}}{(\varepsilon - \tilde{\varepsilon}_f)^2 + \tilde{\Gamma}^2}$$

$$\sqrt{\tilde{\varepsilon}_f^2 + \tilde{\Gamma}^2} \equiv T_K = De^{-\frac{\pi |\varepsilon_f|}{NT\Gamma}}$$

Exact Kondo temperature!!!!
\[ U \rightarrow \infty \]

Double occupancy of the orbitals becomes forbidden.
$U \rightarrow \infty$

Double occupancy of the orbitals becomes forbidden
\[ U \rightarrow \infty \]

Double occupancy of the orbitals becomes forbidden.

Physical explanation

• For \( U=0 \) one would just have a trivial resonant level below the Fermi energy.

• In the presence of interactions, the constraint forces the resonance to be slightly above the Fermi level while at the same time narrowing it: the hopping amplitude is strongly reduced by the interactions, electrons have to “wait” until the level is empty, this job is taken care of by the slave boson that gives the probability of being empty.
The same method applied to the lattice gives the strong renormalization of the heavy fermion bands

\[ E_{k\pm} = \frac{\epsilon_k + \lambda}{2} \pm \left[ \left( \frac{\epsilon_k - \lambda}{2} \right)^2 + |\tilde{V}|^2 \right]^{\frac{1}{2}} \]
Picture confirmed by Dynamical Mean field calculations of the periodic Anderson model

The same method applied to the lattice gives the strong renormalization of the heavy fermion bands

\[ E_{k\pm} = \frac{\epsilon_k + \lambda}{2} \pm \left[ \left( \frac{\epsilon_k - \lambda}{2} \right)^2 + |\tilde{V}|^2 \right]^{\frac{1}{2}} \]
Optical conductivity

According to the f-sum rule, the total integrated optical conductivity is determined by the plasma frequency. In the absence of local moments, this is the total spectral weight inside the Drude peak of the optical conductivity

\[
\frac{2}{\pi} \int_0^\infty d\omega \sigma(\omega) = f_1 = \frac{ne^2}{m}
\]

But what happens to the distribution of the spectral weight when the heavy-electron fluid forms? Physically, while we expect this sum rule to be preserved, a new quasiparticle Drude peak will form, corresponding to the heavy-electron Drude peak

\[
\frac{2}{\pi} \int_0^{TK} d\omega \sigma(\omega) = f_2 = \frac{ne^2}{m^*}
\]
The total spectral weight is divided up into a small “heavy fermion” Drude peak of weight $f_2$ and a large interband component associated with excitations between lower and upper Kondo bands.

\[
\Delta \omega \sim V \sim \sqrt{T_K D}
\]

\[
\left( \frac{V}{T_K} \right)^2 \approx \frac{D}{T_K} \sim \frac{m^*}{m}
\]
\[ \left( \frac{V}{T_K} \right)^2 \approx \frac{D}{T_K} \sim \frac{m^*}{m} \]