Theory of thermoelectric phenomena

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Kondo effect is a common name for a variety of phenomena that occur when degenerate fermions scatter on a degenerate target!

It was first observed in dilute alloys with magnetic impurities.

The effects scale with impurity concentration, so one can speak of 'single impurity effects'.

One can observe how the magnetic impurities affect the conduction states or how the conduction states affect the impurity properties.

In both cases, one finds anomalies.

The thermopower and power factor of Kondo systems can be very large.
Summary of properties

The high-temperature phase (weak coupling regime):

- the impurity behaves as a local moment. The susceptibility is Curie-Weiss and paramagnetic entropy is large.
- conduction states are nearly free; Fermi volume is unaffected by impurities, logarithmic transport coefficients.

The low-temperature phase (strong coupling regime)

Impurity is non-magnetic, there is no paramagnetic entropy. Conduction band is a Fermi liquid:

- power law resistivity
- Pauli like susceptibility
- linear specific heat

The Fermi volume expands with respect to the high-T phase.

The crossover between the two phases occurs at temperature $T_K$. $k_B T_K$ is the only characteristic energy scale of the system.
Kondo effect was first studied in dilute alloys of 3d impurities dissolved in non-magnetic hosts, like Mn in Au or Fe in Cu.

Even though the 3d impurities are difficult to describe by simple models, the early work revealed the basic features of Kondo effect:

- effective coupling changes with temperature or applied field,
- there is a crossover from weak- to strong-coupling behavior,
- the spin entropy is gradually reduced as temperature is lowered.

Particular features depend on:
- The type of impurity:
  the effective degeneracy and splitting of the local states,
- The type of the host:
  the number of itinerant particles (band filling),
- the strength of the coupling between the impurity and the host
Early theoretical developments

Kondo continued the work of Kasuya and Yosida, using the $J \mathbf{s} \cdot \mathbf{S}$ model to describe the interaction between the conduction electrons and magnetic impurity.

Kondo calculated the spin-flip scattering to third order in $J$.

- Perturbation theory explains the high-temperature transport properties of the alloy and the thermodynamic properties of the impurity.
- Kondo explained the resistivity minimum.
- But at low temperatures, perturbation theory predicts: logarithmic resistivity and finite entropy of local moments. This is in contradiction to the experiments.
- Summing all diagrams does not cure the problem.

It soon become clear that the $\mathbf{s} \cdot \mathbf{S}$ model captures the essence of the experiment but the available theoretical tools are not adequate.
The solution of the $s \cdot S$ model was obtained by experimental methods. The data show:

- The cross-section for the scattering of conduction electrons is always finite.

- The susceptibility and the specific heat of local moments saturate at low temperatures. There is no entropy at $T=0$.

Kondo problem, like superconductivity, is non-perturbative. It took several decades to find the full solution.

The qualitative theoretical solution was provided by the Anderson’s poor man’s scaling.

The rigorous solutions were obtained by NRG, Bethe Ansatz, conformal mapping, and renormalized perturbation theory.
Susceptibility follows at high temperatures the Curie-Weiss law

\[ \chi_{\text{imp}}(T) = \frac{1}{3k_B} \frac{\mu_m^2}{T + \Theta_\chi}. \]

At low temperatures, the susceptibility is Pauli like.

\[ \chi_{\text{imp}}(T) = \chi_{\text{imp}}^0 \left[ 1 - B \frac{\pi^2}{3} \left( \frac{T}{\Theta_\chi^0} \right)^2 \right], \quad \Theta_\chi^0 \sim \Theta_\chi. \]

Studying \( \chi_{\text{imp}}(T) \) across the 3d series revealed that \( \chi_{\text{imp}}^0 \) has a peak for Mn and Cr. Such a behavior can be explained by the VBS model, except for the enhancement factor

\[ \chi_{\text{imp}}^0(N_d) = \mu_B^2 \rho_d(E_F) \frac{\Gamma}{k_B \Theta_\chi}, \]

\( \Gamma \) is the width of the VBS,

\( \rho_d(\epsilon) \) is the density of impurity states.
(A) The inverse impurity susceptibility of class (a), (b), and (c) systems plotted as a function of temperature.

Type (a) and (b) behavior – Kondo alloys.
Type (c) behaviour – impurities are decoupled from the conduction see.

(B) The impurity specific heat of a dilute CuCr alloy plotted as a function of temperature.
Entropy and specific heat

At low T, the impurity specific heat is linear, $\Delta C_V(T) = \Delta \gamma T$.

$$\Delta \gamma \simeq k_B^2 \rho_d(\epsilon_F) \frac{\Gamma}{k_B \Theta_{\gamma}}, \quad \Theta_{\gamma} \simeq \Theta_{\chi}.$$  

The enhancement factor is the same as for the susceptibility.

Entropy is given by the integral

$$\Delta S(T) = \int_0^T dT' \frac{\Delta C_V(T')}{T'}.$$  

For an impurity with magnetic moment $\mu_m = g \mu_B \sqrt{S(S+1)}$, the limiting value is $\Delta S|_{T \to \infty} \simeq k_B \ln(2S + 1)$

$$\Delta S(\Theta_{\Delta S}) = k_B/2 \text{ defines } \Theta_{\Delta S} \text{ comparable to } \Theta_{\gamma} \text{ or } \Theta_{\chi}.$$  

The entropy can be removed from the system in two ways.

- If $E_{RKKY} \gg k_B T_K$, entropy is removed by the LRO.
- If $E_{RKKY} \leq k_B T_K$, entropy is quenched by the Kondo effect.
Single impurity limit.

- The impurity resistivity is estimated as \( \Delta \rho(T) = \rho_{\text{alloy}} - \rho_{\text{host}} \).

- The single-impurity resistivity is \( \rho_{\text{imp}}(T) = \Delta \rho/c_i \).

- The residual resistivity is fully explained by the phase shift analysis of the impurity scattering,

\[
\rho_{\text{imp}}^0 = \frac{\Delta \rho(0)}{c_i} = \rho_u \sum_{l=1} l \sin^2[\eta_{l-1}(\epsilon_F) - \eta_l(\epsilon_F)],
\]

Unlike the specific heat and the susceptibility, the resistivity at \( T = 0 \) gives no indication of the anomalies in the middle of the 3d series.
The scattering of conduction electrons on magnetic impurities exhibits different features at low and high temperatures.

- At low temperatures, the resistivity follows a simple power law

\[ \rho_{\text{imp}}(T) = \rho_{\text{imp}}^0 \left[ 1 - \left( \frac{T}{\Theta_\rho} \right)^2 \right], \quad \Theta_\rho \sim \Theta_\chi \]

- For 3-d impurities, the \( l=2 \) phase shift is energy dependent. But the phase shift analysis cannot explain the data for \( T \geq T_K \).

- At high temperatures, the resistivity decreases logarithmically with \( T \).

\( \rho_{\text{imp}} \) plotted versus \( N_d \) looks anomalous at room temperature.
Resistivity of dilute Kondo impurities in various hosts

![Graphs](image)

**Figure:** (A) $\Delta \rho / c_i |_{T=0}$ for some Kondo alloys with $3d$-impurities. If the same figure is drawn for $\Delta \rho / c_i |_{T \geq \Theta}$, we find two peaks and the minimum on Cr or Mn.

(B) Electrical resistivity plotted versus $T / \Theta$ for the same alloys as in (A). The normalization factor $1 / \rho_u$ makes the residual resistance of a given impurity independent of the host.
Thermopower of Kondo alloys

Thermopower is large and independent of the concentration of impurities.

The low-temperature behavior:

- $\alpha(T)$ is linear at low temperature and the slope is

$$\frac{d\alpha}{dT} \simeq \frac{\Gamma}{k_B \Theta_S} \frac{d\rho_d(\epsilon)}{d\epsilon}|_{\epsilon_F}, \quad \Theta_S \simeq \Theta_\rho.$$ 

The phase shift analysis gives the overall trend across the 3-d series but fails to account for the enhancement at Mn and Cr.

- The maximum of thermopower occurs around $\Theta_S$.
  The value at the maximum increases with $\Theta_S$.

The high-temperature behavior

- Thermopower decreases logarithmically with $T/T_S$.

A single parameter $\Theta_S$ characterizes all the regimes.
Thermopower of 3d-alloys

Figure: (A) The initial slope $d\alpha/dT$ for 3d impurities dissolved in Al. (B) Thermoelectric power versus reduced temperature $T/\Theta_\rho$. Open circles: CuFe, $\Theta_\rho = 21$ K; open triangles: AuV, $\Theta_\rho = 280$ K; Open squares: AuCo, $\Theta_\rho \simeq 200$ K; crosses: AlMn, $\Theta_\rho = 530$ K. The normalization factor $1/S_N$ is chosen so that all curves have the same initial slope.
Kondo effect with Cerium and Ytterbium ions

The transport properties of Ce and Yb alloys are similar to 3d alloys but there are some important differences.

Advantage of the 4f with respect to the 3d alloys is that there is only a single f-electron or f-hole in the 4f-shell. The disadvantage is

- because of strong spin-orbit coupling the magnetic quantum number is total angular momentum $j$,
- in a crystalline environment, the degeneracy of the spin-orbit multiplets is reduced because of the CEF effects.
- The CEF splitting provides an additional energy scale.
- Effective degeneracy of the f-state changes with temperature.

The model has to take into account the hierarchy of the energy levels of 4f states.
Energy levels for $f$ electron in Ce$^{3+}$

- $4f^2$
- $4f^1$
- $\varepsilon_f \sim 1\text{ eV}$
- $J=7/2$
- $\Delta_{SO} \sim 0.3\text{ eV}$
- $\Delta_{CEF} \sim 0.01\text{ eV}$
- $U \sim 10\text{ eV}$
Resistivity and thermopower exhibit a two-peak structure. The single-ion properties are concentration dependent, because of chemical pressure (lanthanide contraction). Pressure data are important for theoretical modeling.

**Figure:** Electrical resistivity (A) and thermoelectric power (B) of $\text{Ce}_x\text{La}_{1-x}\text{Cu}_{2.05}\text{Si}_2$ plotted versus temperature for $x \leq 0.09$ samples.
Anderson Hamiltonian of the spin-1/2 impurity:

\[ H_A = H_c + H_{\text{mix}} + H_{\text{imp}} \]

Conduction states

\[ H_c = \sum_{k\sigma} (\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma} \]

Impurity states

\[ H_{\text{imp}} = \sum_{\sigma} (\epsilon_d - \mu) a_{d,\sigma}^\dagger a_{d,\sigma} + U n_{d,\uparrow} n_{d,\downarrow} \]

Single-particle excitation energies of \( H_{\text{imp}} \):

\[ (E_1 - E_0) = \epsilon_d \quad \text{and} \quad (E_2 - E_1) = \epsilon_d + U \]

If \( \epsilon_d < \mu \) and \( \epsilon_d + U > \mu \), impurity is singly occupied.

If both \( \epsilon_d \) and \( \epsilon_d + U \) are below or above \( \mu \), impurity is either doubly occupied or unoccupied.
Hybridization between the conduction and localized states:

\[ H_{\text{mix}} = \sum_{k,\sigma} \left( V_k a_{d,\sigma}^\dagger c_{k,\sigma} + V_k^* c_{k,\sigma}^\dagger a_{d,\sigma} \right), \]

\[ V_k = \langle k | V(r) | d \rangle \]

Limiting behavior of the Anderson model.

- \( U = 0 \) gives the same results as the scattering model with the resonant phase shift. Conduction electrons T-matrix is

\[ T_c(\omega) = V G_d(\omega) V = \frac{V^2}{\omega - (\epsilon_d - \mu) + i\Gamma} \]

and the phase shift

\[ \tan \eta(\omega) = -\frac{\text{Im} G_d(\omega)}{\text{Re} G_d(\omega)} \]

- Atomic limit \( V_k = 0 \) is also easy to solve.

General solution is difficult.
The s-d exchange model

Consider the coupling between spin densities.

\[ H_{sd} = -J(r)s(r) \cdot \mathbf{S} \]

Usually, J is ferromagnetic, \( J > 0 \) and \( H_{sd} \) describes Heisenberg exchange.

Anderson model can be reduced to the s-d model with negative J.

For \( J < 0 \), the antiferromagnetic coupling leads to Kondo effect.

The s-d exchange model:

\[ H_{sd} = - \sum_{k,k'} J_{k,k'} \left[ S^+ c_{k,\downarrow} c_{k',\uparrow} + S^- c_{k,\uparrow} c_{k',\downarrow} + S_z (c_{k,\uparrow} c_{k',\uparrow} - c_{k,\downarrow} c_{k',\downarrow}) \right] \]

Spin operators: \( S_z \) and \( S^\pm = S_x \pm iS_y \).

Kondo Hamiltonian:

\[ H_K = H_c + H_{sd} \]
The properties of the s-d exchange model

The susceptibility of an impurity decoupled from the conduction band is Curie-like

$$\chi_{imp} = g^2 \mu_B^2 \frac{S(S + 1)}{3k_B T}.$$  

The AFM coupling to the conduction band reduces the moment.

The lowest order perturbation theory in the s-d coupling gives,

$$\chi_{imp} = g^2 \mu_B^2 \frac{S(S + 1)}{3k_B T} (1 - 2|J|\rho_0),$$  

Infinite order perturbation theory gives the Curie-Weiss form

$$\chi_{imp} = g^2 \mu_B^2 \frac{S(S + 1)}{3k_B T} \frac{1}{T + T_K}$$  

Fine at high temperatures but wrong at low temperatures.
Consider the case $\epsilon_d \ll \mu$ and $\epsilon_d + U \gg \mu$.

In the ground state, the impurity is singly occupied and magnetic.

\[
H_A = \sum_\sigma \epsilon_d n_{d,\sigma} + Un_{d,\uparrow}n_{d,\downarrow} + \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \sum_{k,\sigma} \left( V_k a_{d,\sigma}^\dagger c_{k,\sigma} + V_k^* c_{k,\sigma}^\dagger d_{d,\sigma} \right)
\]

For $V = 0$, the state vector describes an impurity with 0, 1 or electrons.
For $V \neq 0$, the Hilbert space of $H_A$ is spanned by $H_0$, $H_1$, and $H_2$.
The Schroedinger equation is

\[
H_A \psi = E \psi, \quad \text{where} \quad \psi = (\psi_0, \psi_1, \psi_2).
\]

$\psi_0 \in H_0$, $\psi_1 \in H_1$, and $\psi_2 \in H_2$. Thus, we can write

\[
\begin{bmatrix}
H_{00} & H_{01} & 0 \\
H_{10} & H_{11} & H_{12} \\
0 & H_{21} & H_{22}
\end{bmatrix}
\begin{bmatrix}
\psi_0 \\
\psi_1 \\
\psi_2
\end{bmatrix}
= E
\begin{bmatrix}
\psi_0 \\
\psi_1 \\
\psi_2
\end{bmatrix}
\]

(1)

The off–diagonal terms connect $H_0$, $H_1$, and $H_2$ via the hybridization.
Diagonal terms have no hybridization.
Let’s find an effective Hamiltonian that operates within $\mathcal{H}_1$ and preserves the low-energy structure of the excitations,

$$(H_{11} + \Delta H_{\text{eff}})\psi_1 = E\psi_1,$$

Start from

$$H_{11}\psi_1 + H_{12}\psi_2 + H_{10}\psi_0 = E\psi_1,$$

and eliminate $\psi_0$ and $\psi_2$ using

$$\psi_0 = \frac{1}{E - H_{00}} H_{01}\psi_1,$$

$$\psi_2 = \frac{1}{E - H_{22}} H_{21}\psi_1.$$

The propagation of $\psi_1$ within $\mathcal{H}_1$ is defined by $H_{11}$. But $\psi_1$ propagates also within $\mathcal{H}_0$ and $\mathcal{H}_2$ because of

$$\Delta H = H_{12} \frac{1}{E - H_{22}} H_{21} + H_{10} \frac{1}{E - H_{00}} H_{01}$$

We want to restrict $\psi_1$ to $\mathcal{H}_1$ but keep the same eigenvalues.
Remove the propagation of $\psi_1$ within $\mathcal{H}_0$ and $\mathcal{H}_2$:

$$\frac{1}{E - H_{00}} H_{01} \psi_1 \simeq \frac{1}{E - |\epsilon_d|} H_{01} \psi_1$$

and

$$\frac{1}{E - H_{00}} H_{21} \psi_1 \simeq \frac{1}{E - (\epsilon_d + U)} H_{21} \psi_1.$$  

We neglected the energy of additional conduction particle with respect to the excitation energies of the impurity, when its occupation changed by one. The effective interaction describes propagation within $\mathcal{H}_1$

$$\Delta H_{\text{eff}} = \frac{1}{E - (\epsilon_d + U)} H_{12} H_{21} + \frac{1}{E - |\epsilon_d|} H_{10} H_{01}.$$  

$\Delta H_{\text{eff}}$ takes into account the effect of the high-energy states that are neglected by the effective model and ensures that the eigenvalues are unchanged by the reduction of the Hilbert space.

Substituting for $H_{ij}$ the hybridization terms of $H_A$ and using $E \ll |\epsilon_d|, \epsilon_d + U$, reduces $\Delta H_{\text{eff}}$ to the s-d Hamiltonian,
\[ \Delta H_{\text{eff}} = \sum_{\sigma} \Delta \epsilon_d \ a_{d,\sigma}^\dagger a_{d,\sigma} + \sum_{k,k',\sigma} K_{kk'} c_{k,\sigma}^\dagger c_{k',\sigma} \]

\[ - \sum_{k,k'} J_{kk'} \left[ S_z \left( c_{k,\uparrow}^\dagger c_{k',\uparrow} - c_{k,\downarrow}^\dagger c_{k',\downarrow} \right) + S_+ c_{k,\downarrow}^\dagger c_{k',\uparrow} + S_- c_{k,\uparrow}^\dagger c_{k',\downarrow} \right] , \]

with

\[ \Delta \epsilon_d = \sum_{k} \frac{|V_k|^2}{\epsilon_d} , \quad \text{shift of impurity states} \]

\[ K_{kk'} = -\frac{1}{2} \left( \frac{V_k^* V_{k'}}{\epsilon_d + U} + \frac{V_k^* V_k'}{\epsilon_d} \right) , \quad \text{potential scattering} \]

\[ J_{kk'} = \frac{V_k^* V_{k'}}{\epsilon_d} - \frac{V_k^* V_k'}{\epsilon_d + U} , \quad \text{exchange scattering} \]

Ignoring the impurity term, \( H_{\text{imp}} \), the sum of the conduction-electron Hamiltonian and \( \Delta H_{\text{eff}} \) gives

\[ H_K = H_c + H_{sd} + H_{\text{pot}} . \]

For \( \epsilon_d = -U/2 \) the potential scattering vanishes and \( J < 0 \).
Solution of the Kondo problem by perturbative scaling

Typically, we want to compute the quantum mechanical averages

\[ \langle \hat{O} \rangle = \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{O} \right\} / Z \]

The trace is over the basis states of the Hilbert space of \( \hat{H} \), \( \beta = 1/k_B T \), and \( Z \) is partition function.

In the basis that diagonalizes \( H_c \), the partition function is

\[ Z = \sum_n \langle n | e^{-\beta \hat{H}} | n \rangle. \]

The low-energy states, such that \( E \beta \leq 1 \), appear to be important and one is tempted to neglect the high-energy states.

However, for Kondo model, this would be wrong.

The states close to the band-edge give logarithmic correction to the correlation functions, leading to divergencies for \( D \to \infty \) and \( T = 0 \).
Anderson suggested to reduce the Hilbert space and modify the Hamiltonian, so as to preserve the low-energy part of the spectrum. Since the states close to the band edges cause logarithmic divergencies, we try to eliminate them from the problem.

**Figure:** The high-energy particle and hole states that are removed by reducing the band width by $|\delta D|$ are indicated by shaded rectangles.
The full Hilbert space is spanned by $\mathcal{H}_0, \mathcal{H}_1$ and $\mathcal{H}_2$, such that $\psi_0 \in \mathcal{H}_0$ describes a state with at least one hole in the lower band edge; $\psi_2 \in \mathcal{H}_2$ at least one electron in the upper band edge.

$\psi_1 \in \mathcal{H}_1$ has no electrons excited to $D - |\delta D| < \epsilon_k < D$, or holes excited to $-D < \epsilon_k < -D + |\delta D|$;

For any eigenstate $\psi$

$$H_K \psi = E \psi \quad \text{and} \quad \psi = \{ \psi_0, \psi_1, \psi_2 \}$$

$\mathcal{H}_0, \mathcal{H}_1$, and $\mathcal{H}_2$ are not invariant subspaces of $H_K = H_c + H_{sd}$.

$H_{sd}$ can transfer a state from $\mathcal{H}_1$ to $\mathcal{H}_0$ or $\mathcal{H}_2$, or from $\mathcal{H}_0$ to $\mathcal{H}_2$.

The full Schrödinger equation is

$$
\begin{pmatrix}
H_{00} & H_{01} & H_{02} \\
H_{10} & H_{11} & H_{12} \\
H_{20} & H_{21} & H_{22}
\end{pmatrix}
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2
\end{pmatrix}
= E
\begin{pmatrix}
\psi_0 \\
\psi_1 \\
\psi_2
\end{pmatrix},
$$

We want an effective Hamiltonian that does not take $\psi_1$ out of $\mathcal{H}_1$. 

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Theory of thermoelectric phenomena
The exact Schroedinger equation yields

\[ H_{11}\psi_1 + H_{12}\psi_2 + H_{10}\psi_0 = E\psi_1 \]

\[ \psi_0 = \frac{1}{E - H_{00}} H_{01}\psi_1 + \frac{1}{E - H_{00}} H_{02}\psi_2 \]

\[ \psi_2 = \frac{1}{E - H_{22}} H_{21}\psi_1 + \frac{1}{E - H_{22}} H_{20}\psi_0. \]

Eliminating \( \psi_2 \) from the equation for \( \psi_0 \) gives

\[ \psi_0 = \left( \frac{1}{E - H_{00}} H_{01} + \frac{1}{E - H_{00}} H_{02} \right) \frac{1}{E - H_{22}} H_{21} \psi_1 + \frac{1}{E - H_{00}} H_{02} \frac{1}{E - H_{22}} H_{20} \frac{1}{E - H_{00}} H_{01} + \cdots \right) \psi_1, \]

Eliminating \( \psi_0 \) from the equation for \( \psi_2 \) gives a similar expression which relates \( \psi_2 \) to \( \psi_1 \).

We now want to eliminate the propagation of \( \psi_1 \) within \( \mathcal{H}_0 \) and \( \mathcal{H}_2 \).
Since $H_{00}\psi_0 \in \mathcal{H}_0$ and $H_{22}\psi_2 \in \mathcal{H}_2$, and $E, |J| \ll D$, we approximate

$$\frac{1}{E - H_{00}} H_{01}\psi_1 \simeq \frac{1}{E - H_c} H_{01}\psi_1 \equiv \frac{H_{01}}{|D|} \psi_1$$

and

$$\frac{1}{E - H_{22}} H_{21}\psi_1 \simeq \frac{1}{E - H_c} H_{21}\psi_1 \equiv \frac{H_{21}}{|D|} \psi_1$$

Each successive term for $\psi_0$ and $\psi_2$ has one more power of $1/D$.

To lowest order in $1/D$,

$$(H_{11} + \Delta H)\psi_1 = E\psi_1$$

and

$$\Delta H = H_{10} \frac{1}{|D|} H_{01} + H_{12} \frac{1}{|D|} H_{21}.$$ 

Effective Hamiltonian $H_{11} + \Delta H$ operates in a reduced Hilbert space $\mathcal{H}_1$ and has the same low-energy spectrum as $H_K$.

Let’s find the explicit expression for $\Delta H$. 
The corrections $H_{10}H_{01} + H_{12}H_{21}$ are due to the exchange scattering

$$H_{sd} = \sum_{k,k'} \left[ -J_+ S^+ c_{k,\downarrow}^\dagger c_{k',\uparrow} - J_- S^- c_{k,\uparrow}^\dagger c_{k',\downarrow} - J_z S_z (c_{k,\uparrow}^\dagger c_{k',\uparrow} - c_{k,\downarrow}^\dagger c_{k',\downarrow}) \right]$$

The corrections can be represented graphically
The processes shown in (A) renormalize $-J_z$: an electron scatters from $k \uparrow$ into $q \downarrow$ and then to a final state $k' \uparrow$. The $q$- and $q'$-states are within the band edges, $\epsilon_q, \epsilon_{q'} \simeq D$.

The contribution to $\Delta H$ is

$$J_+ J_- \sum_q S^- c_{k', \uparrow} ^\dagger c_{q, \downarrow} \frac{1}{E - H_c} \sum_{q'} S^+ c_{q', \downarrow} ^\dagger c_{k, \uparrow}.$$ 

At low temperatures the band edges are unoccupied, so $c_{q, \downarrow} ^\dagger c_{q', \downarrow} = \delta_{q,q'}$ and

$$(J_+ J_-)(S^- S^+) \sum_q \frac{1}{E - (E_0 + \epsilon_q - \epsilon_k)} c_{k', \uparrow} ^\dagger c_{k, \uparrow}.$$ 

$E_0$ is the energy of the initial state. Summing over all $q$-states and using $S^- S^+ = 1/2 - S_z$ model, gives

$$\Delta H^{(A)} = \frac{J_+ J_- \rho_0 |\delta D|}{\Delta E - D + \epsilon_k} (1/2 - S_z)c_{k, \uparrow} ^\dagger c_{k', \uparrow}.$$ 

(2)
Processes shown in (B) also renormalize $J_z$ and contribute to $\Delta H$

$$\Delta H^{(B)} = -\frac{J_+ J_- \rho_0 |\delta D|}{\Delta E - D - \epsilon_{k'}} \left(1/2 + S_z\right) c_{k'}^\dagger c_k^\uparrow, \uparrow$$

The sum (over spins) of all these processes gives the change of $J_z$,

$$\delta |J_z| = -J_+ J_- \rho_0 |\delta D| \left(\frac{1}{\Delta E - D + \epsilon_k} + \frac{1}{\Delta E - D - \epsilon_{k'}}\right).$$

Processes shown in (C) and (D) describe the spin-flip scattering

$$-\frac{1}{2} \frac{J_+ J_z \rho_0 |\delta D|}{\Delta E - D + \epsilon_k} S^+ c_{k'}^\dagger, \downarrow c_k^\uparrow, \uparrow \quad \text{and} \quad \frac{1}{2} \frac{J_+ J_z \rho_0 |\delta D|}{\Delta E - D - \epsilon_{k'}} S^+ c_k^\uparrow c_{k'}^\dagger, \downarrow$$

The sum of all such processes gives the change of $J_\pm$

$$\delta |J_\pm| = -J_\pm J_z \rho_0 |\delta D| \left(\frac{1}{\Delta E - D + \epsilon_k} + \frac{1}{\Delta E - D - \epsilon_{k'}}\right).$$
The effective Hamiltonian is operating in reduced Hilbert space with the cutoff $D - |\Delta D|$.

$H_{11} + \Delta H$ has the same form as the initial Kondo Hamiltonian but the coupling constant are renormalized.

The low-energy excitations are invariant with respect to the reduction of $D$, provided the coupling constants are rescaled as

$$\frac{d|J_\pm|}{d \ln D} = -2\rho_0 J_z J_\pm \quad \text{and} \quad \frac{d|J_z|}{d \ln D} = -2\rho_0 J_\pm^2,$$

with the initial condition $J_\pm(D_0) = J^0_\pm$ and $J_z(D_0) = J^0_z$.

The anisotropic couplings satisfy

$$dJ_\pm^2 - dJ_z^2 = 0$$
Analysis of the scaling equations for the isotropic model

For $J_{\pm} = J_z = J$, the scaling equation reads

$$\frac{d |J|}{2 \rho_0 J^2} = -d \ln D$$

and the initial condition is $J(D_0) = J_0$. The solution is

$$\ln D - \frac{1}{2 \rho_0 |J|} = \ln D_0 - \frac{1}{2 \rho_0 |J_0|} \equiv \ln (k_B T_K)$$

$J(D)$ depends on initial parameters only through scaling invariant $T_K$.

$T_K$ is defined as the band width at which $J = \infty$,

$$k_B T_K = D_0 \exp \left( -\frac{1}{2 |J_0| \rho_0} \right)$$

$T_K$ is not an analytic function of $J_0$ and $T_K(J_0)$ cannot be obtained by the perturbation theory in $J_0$.

Higher order scaling does not change the exponential form of $T_K$ but just modifies the prefactor.
Physical properties derived by scaling

Each $T_K$ defines a scaling trajectory $J(D, T_K)$.
Reducing $D \rightarrow A k_B T$ ($A$ is parameter-independent constant).

For $A \approx 1$

$$2\rho_0 |J(T)| = \frac{1}{\ln(T/T_K)}$$

$J(T) \rightarrow 0$ for $T \rightarrow \infty$.

For $T > T_K$, the conduction band is finite and the response functions can be obtained by perturbation theory in $J$, provided $|J(T)| < 1$.

Magnetic susceptibility

$$\chi_{\text{imp}}(T) = \frac{\mu^2_S}{3 k_B T} [1 - 2\rho_0 |J(T)|] = \chi_{\text{ion}}(T) \left[1 - \frac{1}{\ln(AT/T_K)}\right]$$

The effective moment decreases as temperature approaches $T_K$.

For $T_K < T \ll 100 \ T_K$, we can also write

$$\chi_{\text{imp}}(T) \simeq \frac{\mu^2_S}{3 k_B} \frac{C}{T + \Theta}$$
Kondo coupling reduces the impurity entropy with respect to the free-ion high-temperature value $S_{\text{imp}}^0 = k_B \ln(2S + 1)$.

For $S_{\text{imp}} = (\partial F / \partial T)|_V$, the lowest order perturbation theory gives

$$S_{\text{imp}}(T) = k_B \ln(2S + 1) \left[ 1 - \frac{\pi^2}{3} \frac{1}{\ln^3(\frac{AT}{TK})} \right],$$

the specific heat

$$C_{\text{imp}}(T) = \pi^2 k_B \ln(2S + 1) \frac{\ln(\frac{AT}{TK})}{[\ln(\frac{AT}{TK})]^4}.$$ 

Scaling extends the range of validity of the perturbation theory.

The scaling agrees with the results obtained by the diagrammatic perturbation theory taken to infinite order.

The susceptibility and the entropy agree with the result obtained by the parquet summation of diagrams.
For impurity scattering, the transport relaxation time $\tau(\omega)$ is given by the conduction electrons $T$-matrix.

Using for the $T$-matrix the lowest order Born approximation and calculating the transport coefficients by the Boltzmann theory gives, for $T > T_K$,

$$\frac{\rho_{\text{imp}}(T)}{c_i R_0} = \left\{ (\rho_0 V)^2 + S(S + 1)[\rho_0 J(T)]^2 \right\} = \left\{ (\rho_0 V)^2 + \frac{S(S + 1)}{[\ln(T/T_K)]^2} \right\}$$

$V$ is the strength of the potential scattering.

The resistivity increases as $T$ approaches $T_K$.

The same logarithmic dependence is obtained by extending the order of the perturbation theory to infinity.
For $V = 0$, the model is symmetric and transport integral $L_{12}$ is zero.

Potential scattering makes the Kondo model asymmetric and the interference between $V$ and $J$ gives for $S = 1/2$

$$\alpha_{\text{imp}}(T) = 2\pi^2 \left( \frac{k_B}{e} \right) \frac{(\rho_0|J|)(\rho_0V)}{(\rho_0|J|)^2 + (\rho_0V)^2}.$$  

Potential scattering is not renormalized by scaling. Using for $J(T)$ the scaling result gives

$$\alpha_{\text{imp}}(T) \sim \left( \frac{k_B}{e} \right) \frac{1}{\rho_0 V \ln(T/T_K)} \frac{1}{1 + 1/[\rho_0 V \ln(T/T_K)]^2}.$$  

The lowest order correction is

$$\alpha_{\text{imp}}(T) \sim \left( \frac{k_B}{e} \right) \frac{1}{\rho_0 V \ln(T/T_K)} \left[ 1 - \frac{1}{[\rho_0 V \ln(T/T_K)]^2} \right].$$  

$|\alpha_{\text{imp}}(T)|$ increases as temperature is lowered towards $T_K$.

The sign of $\alpha_{\text{imp}}(T)$ depends on $V$. 

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The scaling solution describes the crossover from the weak coupling regime at high temperatures ($\rho_0 J \to 0$) to the strong coupling regime at low temperatures ($\rho_0 J \to \infty$).

Perturbative scaling breaks down when $T \to T_K$, because the assumptions used to derive the scaling equations cease to hold.

Also, when $J(T)$ is too big, the perturbation theory for the correlation functions cannot be used.

There are difficulties applying the $s=1/2$ Kondo model to real materials.

For 3d impurities the Kondo effect is seen for Mn and Cr, where the exchange model is too simple.

For Ce and Yb impurities, the spin-orbit coupling and the CEF splitting have to be included. The ensuing Coqblin-Schrieffer model can be solved by scaling.
Consider an impurity with two CF levels separated by an energy $\Delta$.

$N_m$ and $N_M$ are the degeneracies of the lower and the upper CF level, $N = N_m + N_M$ is the total degeneracy.

The impurity is represented by the Hamiltonian

$$H_{\text{imp}} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_M \epsilon_M a_M^\dagger a_M$$

The elastic and inelastic transition between the CF states are described by the generalized s-d exchange model

$$H_{\text{ex}} = -J_0 \sum_{k,k',m,m'} c_{k,m}^\dagger c_{k',m'}^\dagger a_{m'} a_m - J_1 \sum_{k,k',M,M'} c_{k,M}^\dagger c_{k',M'}^\dagger a_{M'} a_M$$
$$-J_2 \sum_{k,k',m,M} c_{k,m}^\dagger c_{k',m} a_M^\dagger a_M - J_2 \sum_{k,k',m,M} c_{k,m}^\dagger c_{k',M} a_M^\dagger a_m.$$ 

For Ce ions restricted to the $4f^{11}$ configuration, we have the constraint

$$\sum a_m^\dagger a_m + \sum_a^\dagger a_M = 1.$$
For $T \gg \Delta$, the impurity state is $N$-fold degenerate. The moment is

$$\mu_J = g_J\mu_B \sqrt{J(J+1)}$$

and

$$\chi_{\text{imp}}(T) \simeq (g_J\mu_J)^2 / T$$

At lower temperatures, the susceptibility deviates from Curie form. The qualitative behavior is explained by scaling.
When the width of the conduction band is reduced, the low-energy eigenstates remain unchanged, if the coupling constant changes as

\[ \delta(\rho_0|J|) = -N_m(\rho_0|J|)^2 \frac{\delta D}{D} - N_M(\rho_0|J|)^2 \frac{\delta D}{D + \Delta}. \]

The 1st term on the RHS is due to the scattering on the lower CF level. The 2nd term is due to the scattering on the upper CF level.

Integrating between \( D \) and \( D_0 \) gives the scaling invariant

\[ -\frac{1}{\rho_0|J(D)|} + N_m \ln D + N_M \ln (D + \Delta) = -\frac{1}{\rho_0|J_0|} + N_m \ln D_0 + N_M \ln (D_0 + \Delta). \]

The band width at which \( J(D) \to \infty \) defines the Kondo scale \( T_K \),

\[ \left( \frac{k_B T_K}{D_0} \right)^{N_m} \left( \frac{k_B T_K + \Delta}{D_0 + \Delta} \right)^{N_M} = \exp \left( -\frac{1}{\rho_0|J_0|} \right). \]
Limiting properties of the scaling solution

Limiting behavior \( (N = N_m + N_M) \)

- Small splitting, \( \Delta \ll k_B T_K \),

\[
\frac{k_B T_K}{D_0} = \frac{k_B T_K^{(N)}}{D_0} = \exp \left( -\frac{1}{N \rho_0 |J_0|} \right),
\]

\( T_K \) is the same as the Kondo scale of an \( N \)-fold degenerate state.

- Large splitting, \( \Delta \gg k_B T_K^{(N)} \) (physically relevant case)

\[
T_K = \left( \frac{k_B T_K^{(N)}}{\Delta} \right)^{N_M/N_m} T_K^{(N)}
\]

The CF splitting reduces the Kondo scale, \( T_K \ll T_K^{(N)} \)
Reducing $D$ down to $Ak_B T$ yields the scaling trajectory

$$\exp \left[ -\frac{1}{\rho_0 |J(T)|} \right] = \left( \frac{k_B T_K}{AT} \right)^{N_m} \left( \frac{k_B T_K + \Delta}{AT + \Delta} \right)^{N_M},$$

For given $T_K, \Delta, N_m$ and $N_M$, $J(T)$ defines the properties of the model.

Define the Kondo temperature of a $N_m$-fold degenerate local moment (no CF splitting),

$$\frac{k_B T_K^{(m)}}{D_0} = \exp \left( -\frac{1}{N_m \rho_0 |J_0|} \right)$$

For a CF split state, we have

$$T_K = \left( \frac{D_0}{\Delta} \right)^{N_M/N_m} T_K^{(m)}$$

$T_K$ of a CF split state is much enhanced with respect to $T_K^{(m)}$.

Even for $T \ll \Delta$, the virtual excitations to the high-energy CF states greatly enhance the Kondo scale.

This is the reason that $T_K \simeq 1 - 20 \text{ K}$ for Ce and Yn ions.
Let us look at the susceptibility data on dilute Ce\(_x\)La\(_{1-x}\)Cu\(_{2.05}\)Si\(_2\) alloys,

\[
\chi_J(T) = \frac{[2\chi_{ab}^J(T) + \chi_c^J(T)]}{3}
\]

The lowest order perturbation theory gives

\[
\chi_{ab}^{(c)}(T) = \chi_{CF}^{ab(c)}(T)[1 - 2\rho|J(T)|],
\]

We calculated \(\chi_{CF}^{ab(c)}(T)\) for a tetragonal point group symmetry and used the scaling expression for \(J(T)\).

The solution with \(T_K = 8.5\) K and \(A = 3\) fits the data above 30 K.

At low temperatures, where \(J(T) \simeq J^{(2)}(T)\), the impurity behaves as an effective doublet with \(T_K = 8.5\) K.

The CF theory gives \(\mu_{\text{eff}} = 1.62\mu_B\), not too far from \(\mu_{\text{free}} = \sqrt{3}\mu_B\).

Below 30 K we fit the data using the exact solution of the spin-1/2 model

\[
\chi_W = \frac{0.68C_0}{T + \sqrt{2}T_K}
\]

\(C_0 = 0.375\) emu/mol for S=1/2.
Figure: The inverse of the average single-ion susceptibility shown as a function of temperature for $\text{Ce}_x\text{La}_{1-x}\text{Cu}_{2.05}\text{Si}_2$ samples with $x \leq 0.09$. The dashed line is the CF result and the full line is the scaling result.
Figure: The average single-ion susceptibility of Ce$_x$La$_{1-x}$Cu$_{2.05}$Si$_2$ defined as $\chi_{\text{ion}}(T) = [\chi(x, T) - \chi(0, T)]/x - 10^{-4}$ emu/mol Ce, plotted versus temperature for $x \leq 0.09$ samples. The full line shows the scaling result, the dashed line shows the CF result, and the dashed-dotted line shows the exact solution for the spin-1/2 Kondo model in the local moment regime.