Spectroscopic properties of mixed valence compounds in the impurity model

or

On the history of the single impurity Anderson model and the Kondo resonance

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Outline

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- What is the Kondo resonance?
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systems and models

In this lecture I adress **systems** like

- noble metals with (dilute) “magnetic impurities” (e.g. Co in Au)
- **mixed valence systems (e.g. Cerium compounds)**
- ...

The theoretical description uses **models** like

- the **single impurity Anderson model (SIAM)**
- SIAM with an additional **core level**
- ...

What is the Kondo resonance ?

The existence of what is now usually called **“Kondo resonance”** was conjectured in 1965 independently by **A.A. Abrikosov** and **H. Suhl** (...the singularity is replaced by a resonant scattering close to the Fermi level...). It is therefore also called the **“Abrikosov-Suhl resonance”**.

It is a possible **nontrivial many-body feature** in the spectral function of the one-particle Green’s function of the magnetic impurity at “very low temperatures” with interesting experimental manifestations.

No controlled method to actually calculate it was available till the **early eighties**.

Is there a *simple* way to understand it ?

Prehistory of the SIAM : localized level coupled to a continuum

(K. O. Friedrichs, Commun. Pure Appl. Math **1**, 361 (1948) → **Friedrichs model**)

The localized d-level $|d\rangle$ couples to a a continuum of states $|\epsilon\rangle$.

The single particle Hamiltonian h reads

$$h = \epsilon_d |d\rangle\langle d| + \int \epsilon |\epsilon\rangle\langle\epsilon| d\epsilon + \int \left[V(\epsilon)|d\rangle\langle\epsilon| + H.c. \right] d\epsilon$$

The important **resolvent matrix elements** $g_{ij}(z) \equiv \langle i|(z-h)^{-1}|j\rangle$ are easily calculated multiplying $(z-h)g(z)|d\rangle = |d\rangle$ from the left with $\langle d|$ and $\langle\epsilon|$

$$(z-\epsilon_d)g_{dd}(z) - \int V(\epsilon) g_{\epsilon d}(z) d\epsilon = 1 \ , (z-\epsilon)g_{\epsilon d}(z) - V(\epsilon)^* g_{dd}(z) = 0 \ .$$

Therefore the **local** diagonal element is given by

$$g_{dd}(z) = \frac{1}{z-\epsilon_d-\Gamma(z)} \ , \qquad \Gamma(z) = \int \frac{|V(\epsilon)|^2}{z-\epsilon} d\epsilon \ .$$

SIAM : **the full model** (spin-degenerate)

In order to study a **single magnetic impurity** in simple metals P. W. Anderson proposed the Hamiltonian

$$H_A = \sum_\sigma \left[\epsilon_d n_{d\sigma} + \sum_k \epsilon_k n_{k\sigma} + \sum_k (V_{dk} \psi^\dagger_{d\sigma} \psi_{k\sigma} + H.c.) \right] + U n_{d\uparrow} n_{d\downarrow} \ ,$$

where $\psi_{d,\sigma}$ is the annihilation operator of the localized impurity $|d\rangle$-state with energy ϵ_d and the $\psi_{k,\sigma}$ are the annihilation operators of the delocalized band states $|k\rangle$ with energy ϵ_k. The $n_{d\sigma} = \psi^\dagger_{d\sigma}\psi_{d\sigma}$ (and $d \to k$) are particle number operators. In the body of his 1961 paper Anderson used the "physically unrealistic case" with only spin degeneracy and treated the case of a doubly degenerate "d"-orbital in an appendix. As a "physically realistic" case the spin-degenerate model was later used to describe hydrogen chemisorption on metal surfaces ($d \to a$ for "adsorbate"), where $|a\rangle$ corresponds to the hydrogen $1s$-level (Newns 1965).

The last term of the Anderson Hamiltonian describes the local "Coulomb" repulsion U which acts when the d-level is doubly occupied. This two-body interaction makes the model highly non-trivial.

Technicalities: Green's functions

One can use either "time"-ordered or **retarded** ("Zubarev") Green's functions.

The retarded ones are generally defined as

$$\langle\langle A; B\rangle\rangle_z \equiv -i \int_0^\infty \langle [A(t), B]_\pm \rangle e^{izt} dt \ ,$$

where $A(t) = e^{iHt} A e^{-iHt}$ is the operator A in the Heisenberg picture, $\langle\ \rangle$ denotes the average over the grand canonical ensemble, and z is a complex variable with $\mathrm{Im} z > 0$ in order to ensure the convergence of the time integral. For operators A involving products of and odd (even) number of Fermion field operators the anticommutator $[\ ,\ ]_+$ (commutator $[\ ,\ ]_-$) is chosen. The Heisenberg equation of motion (EOM) for $A(t)$ and a partial integration yields the EOM

$$z\langle\langle A; B\rangle\rangle_z - \langle\langle [A, H]; B\rangle\rangle_z = \langle [A, B]_\pm \rangle \ .$$

This EOM is very useful for discussing the **exactly solvable limits** of the Anderson impurity model.

One-particle Green's function of the interacting model

For interacting systems in the **groundstate** experimentally relevant spectral functions are obtained from the (retarded) **one-particle Green's functions** defined as $G^{(r)}_{i\sigma,j\sigma}(z) \equiv \langle\langle \psi_{i\sigma}; \psi^\dagger_{j\sigma}\rangle\rangle_z$. It can be written in terms of many-body resolvents operators as $(i, j \to d)$

$$G^{(r)}_{d\sigma,d\sigma}(z) = \langle E_0(N)| \left[\psi^\dagger_{d\sigma} \frac{1}{z + H - E_0(N)} \psi_{d\sigma} + \psi_{d\sigma} \frac{1}{z - H + E_0(N)} \psi^\dagger_{d\sigma} \right] |E_0(N)\rangle$$

The first term is relevant for photoemission and the second for inverse photoemission. At finite temperatures one has to average over the initial eigenstates with the appropriate Boltzmann factors. The spectral functions are obtained as

$$\rho^<_{dd}(\epsilon) = -\frac{1}{\pi} f(\epsilon) \mathrm{Im} G^{(r)}_{d\sigma,d\sigma}(\epsilon + i0) \ , \quad \rho^>_{dd}(\epsilon) = -\frac{1}{\pi}(1 - f(\epsilon)) \mathrm{Im} G^{(r)}_{d\sigma,d\sigma}(\epsilon + i0)$$

with $f(\epsilon) = (e^{\beta\epsilon} + 1)^{-1}$ the Fermi function. This leads to

$$\rho^>_{dd}(\epsilon) = e^{\beta\epsilon} \rho^<_{dd}(\epsilon) \quad \text{``photoemission determines inverse photoemmision''},$$

which unfortunately is practically not very useful (see later).

Exactly solvable limits of the SIAM

For $U = 0$ the Anderson impurity model describes noninteracting electrons. For $V = 0$ (no coupling to the host) one is in the atomic limit which allows an exact solution for arbitrary values of U. The Green's functions of both limits can easily be obtained using the equations of motion (EOMs). The beginning of the **infinite hierarchy** of EOMs reads (upper index (r) suppressed)

$$(z - \epsilon_d)G_{d\sigma,d\sigma}(z) - U\langle\langle\psi_{d\sigma}n_{d-\sigma};\psi^\dagger_{d\sigma}\rangle\rangle_z - \sum_k V_{dk}G_{k\sigma,d\sigma}(z) = 1 \ .$$

This requires to write down the EOMs for the **two new funtions** appearing

$$(z - (\epsilon_d + U))\langle\langle\psi_{d\sigma}n_{d-\sigma};\psi^\dagger_{d\sigma}\rangle\rangle_z - \langle\langle[\psi_{d\sigma}n_{d-\sigma}, V];\psi^\dagger_{d\sigma}\rangle\rangle_z = \langle n_{d-\sigma}\rangle \ ,$$

where V is the coupling part of the Hamiltonian. The EOM for $G_{k\sigma,d\sigma}$ reads

$$(z - \epsilon_k)G_{k\sigma,d\sigma}(z) - V^*_{dk}G_{d\sigma,d\sigma}(z) = 0 \ .$$

For $U = 0$ these equations close and one obtains

$$G^{U=0}_{d\sigma,d\sigma}(z) = \frac{1}{z - \epsilon_d - \Gamma(z)}, \quad \text{with} \quad \Gamma(z) = \sum_k \frac{|V_{dk}|^2}{z - \epsilon_k} \quad .$$

Also for $V = 0$ these equations close and one obtains

$$G^{V=0}_{d\sigma,d\sigma}(z) = \frac{1 - \langle n_{d-\sigma} \rangle}{z - \epsilon_d} + \frac{\langle n_{d-\sigma} \rangle}{z - (\epsilon_d + U)}$$

The corresponding spectral function in this atomic limit has sharp atomic peaks at ϵ_d and $\epsilon_d + U$. The most interesting case is when ϵ_d is below the Fermi energy and $\epsilon_d + U$ is above it. An important special case is **particle-hole symmetry**

$$\epsilon_d + \frac{U}{2} = \mu = \epsilon_F (= 0)$$

and a band symmetric around the Fermi energy ϵ_F. In this case

$$G^{V=0}_{d\sigma,d\sigma}(z) = \frac{1/2}{z - \epsilon_d} + \frac{1/2}{z - (\epsilon_d + U)}$$

holds for all temperatures.

Finite V and U: Historical remarks

Reviewing the attempts to find a proper solution to the SIAM is like following the progress in the **quantum many body problem** in general. Here I cannot list them all:

- Hartree-Fock (only a starting point)
- equations of motion (truncation, factorization) uncontrolled
- perturbation theory in U
- perturbation theory in V (no Wick theorem)
- phenomenological Fermi liquid theory
- various renormalization group approaches
- numerical renormalization group (NRG) ("exact" numerical results)
- Bethe ansatz (exact analytical solution, but (so far) **no** spectral functions)
- $1/N_f$ methods: NCA, **"intermediate states method"**: details will be presented as **suggested by the organizers**
- quantum Monte Carlo

There is still **no** "quick and easy" method to obtain the "exact" spectral function for all ϵ.

The Hartree-Fock approximation (HF)

In his 1961-paper Anderson used the HF-approximation. It can be obtained in various ways

- **mean field approximation**:

$$U n_{d\uparrow} n_{d\downarrow} \to U \left(n_{d\uparrow} \langle n_{d\downarrow} \rangle^{HF} + n_{d\downarrow} \langle n_{d\uparrow} \rangle^{HF} - \langle n_{d\uparrow} \rangle^{HF} \langle n_{d\downarrow} \rangle^{HF} \right) \ ,$$

- **diagramatically** (see below)
- **simple factorization**

$$\langle\langle \psi_{d\sigma} n_{d-\sigma}; \psi^\dagger_{d\sigma} \rangle\rangle_z \to \langle n_{d-\sigma} \rangle \langle\langle \psi_{d\sigma}; \psi^\dagger_{d\sigma} \rangle\rangle_z \ .$$

One always obtains

$$G^{HF}_{d\sigma,d\sigma}(z) = \frac{1}{z - \epsilon_d - U\langle n_{d-\sigma} \rangle - \Gamma(z)} \ .$$

with $\langle n_{d-\sigma} \rangle$ to be determined **self-consistently**.

In the **ph-symmetric case**

$$\langle n_{d-\sigma}\rangle^{RHF} = 1/2 = \langle n_{d-\sigma}\rangle^{exact}$$

and the R(estriced)HF resonance is **at the chemical potential**. The shape and position of this RHF-spectral function is **independent** of the value of U in this particle-hole symmetric case.

As discussed by Anderson in his 1961 paper, for U larger than the **critical value** $U_c = \pi\Gamma$ solutions of the HF-equations occur where the occupancies of the impurity level for spin-up and spin-down **differ**. These "**unrestricted Hartree-Fock**" (UHF) solutions are an **artefact of the approximation** as no spontaneous symmetry breaking can occur when the interaction acts in a zero dimensional system.

Therefore the spin variable in the Green's function is suppressed in (most of) the following (e.g. $d\sigma \to d$).

Perturbation theory in U: Fermi liquid property

The perturbation theory (to all orders) in U can be done with usual Feynman diagrams as used by Landau to give a microscopic “proof” of his phenomenological Fermi liquid theory. An important step is to introduce the **selfenergy** $\Sigma(\epsilon)$

$$G_{dd}(z) = \frac{1}{z - \epsilon_d - \Gamma(z) - \Sigma(z)} \; .$$

The first order contribution to Σ in U is just the HF-term $U\langle n_{d,-\sigma}\rangle$.

In the **ph-symmetric case** and a constant $\Gamma(\epsilon + i0) = -i\Gamma$ (“wide band limit”) the spectral function takes the form ($\tilde{\Sigma} \equiv \Sigma - U\langle n_{d,-\sigma}\rangle$)

$$\rho_{dd}(\epsilon) = \frac{1}{\pi} \frac{\Gamma + |\mathrm{Im}\tilde{\Sigma}(\epsilon + i0)|}{(\epsilon - \mathrm{Re}\tilde{\Sigma}(\epsilon))^2 + (\Gamma + |\mathrm{Im}\tilde{\Sigma}(\epsilon + i0)|)^2}$$

with $\mathrm{Re}\tilde{\Sigma}(\epsilon)$ an **even function** of ϵ and the zero temperature **Fermi liquid property** $\mathrm{Im}\tilde{\Sigma}(\epsilon + i0) \sim \epsilon^2$ for $\epsilon \to 0$ holds. This implies the **exact** result

$$T = 0 : \quad \rho_{dd}(0) = \rho_{dd}^{(RHF)}(0) = \frac{1}{\pi\Gamma}$$

For $U/\pi\Gamma \ll 1$ the exact $\rho_{dd}(\epsilon)$ differs only slightly from RHF-solution for $\epsilon \neq 0$. What happens for $U/\pi\Gamma \gg 1$?

Perturbation theory in V: no Wick's theorem

Now the starting point is the **atomic limit**. Due to the Coulomb interaction term in the corresponding zeroth order Hamiltonian a straightforward diagramatic analysis using Wick's theorem is **not** possible.

One possible approach is to introduce the **two modified annihilation operators**

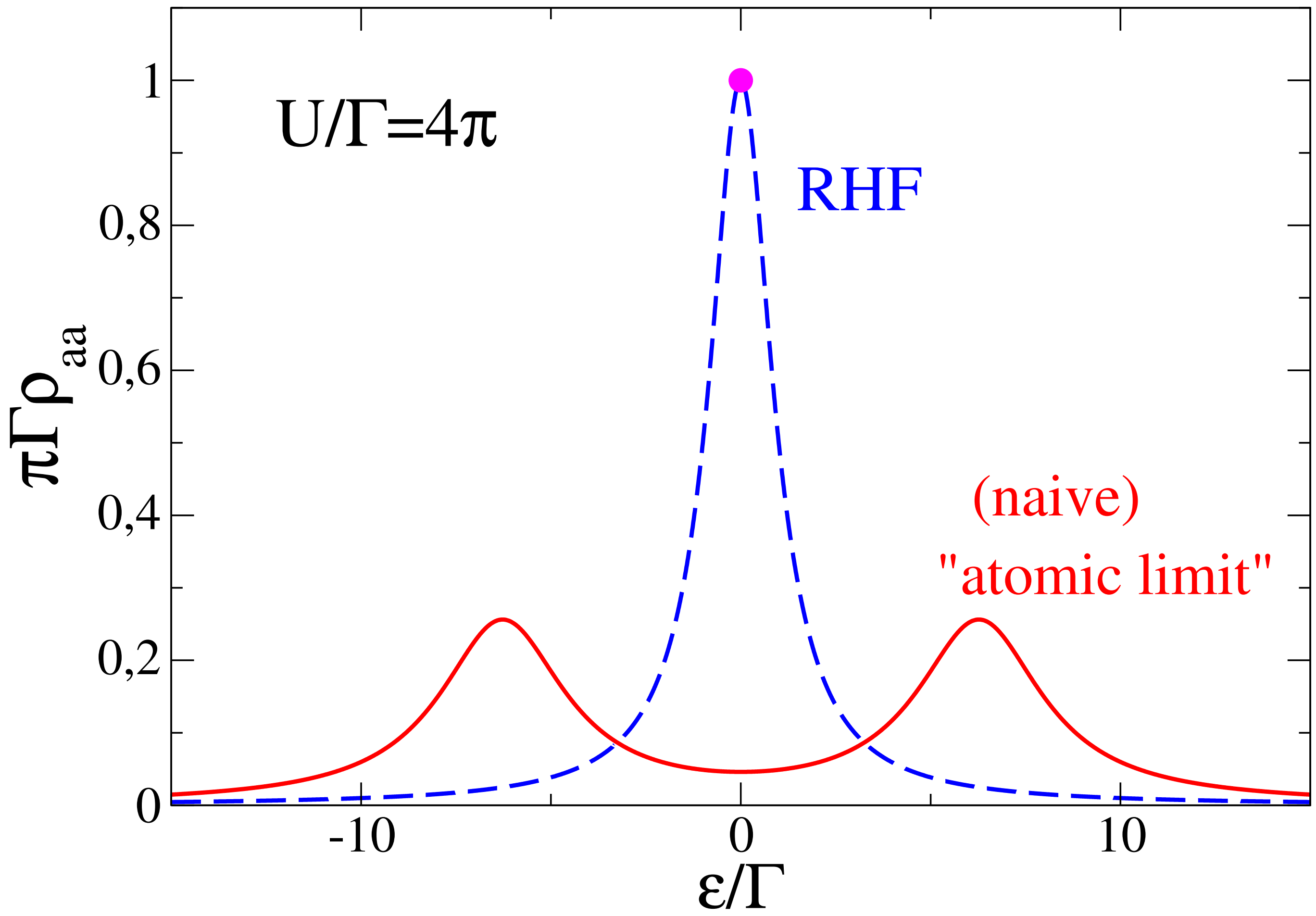
$$\psi_{+,\sigma} \equiv \psi_{a\sigma} n_{a-\sigma} \qquad \psi_{-,\sigma} \equiv \psi_{a\sigma}(1 - n_{a-\sigma})$$

and introduce a 2×2 **matrix self-energy** (W. Brenig, K.S., Z. Phys. **267**, 201 (1974)). Using the EOMs this self-energy is easily calculated to second order in V. In the **ph-symmetric case** this approximately yields

$$G_{dd}(z) \approx \frac{1/2}{z - U/2 - 2\Gamma(z)} + \frac{1/2}{z + U/2 - 2\Gamma(z)} \ .$$

If an electron is removed from the impurity level the empty impurity state created can decay by tunneling back in of a spin-up **or** spin-down electron which gives the "atomic peaks" a **width twice as large** as the width of the RHF-Lorentzian.

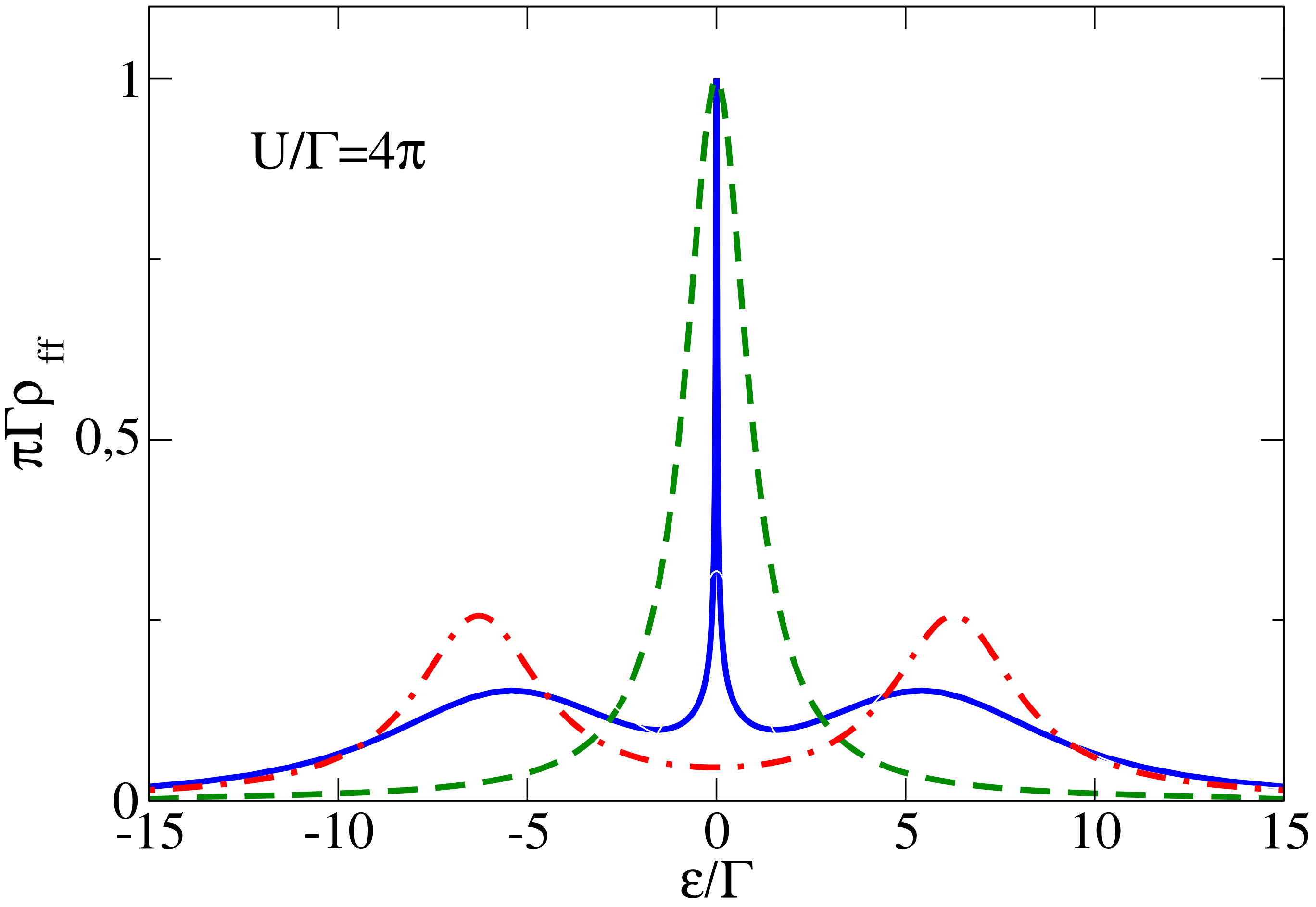
We now have **two** **(naive!?)** **approximate solutions**



What is the exact result for the spectral function?

For $U/\pi\Gamma \gg 1$ almost all weight is in the "atomic resonances". This implies a **very narrow resonance** at the chemical potential $\epsilon = 0$.

It was only in the second half of the eighties that a (numerically) exact solution for the spectral function was available (NRG, see later)



What is the exact position of this **Kondo resonance** **away form the ph-symmetric case?**

Before addressing this question systems (models) with an additional **core level** are discussed.

Impurity models involving a core level

X-ray photoemission spectroscopy (XPS) of **core levels of an impurity** as well as X-ray absorption spectroscopy are useful tools to obtain **information about the properties of the valence electrons.**

In a **minimal model** a **single nondegenerate core level** of the impurity with energy ϵ_c is considered which is **filled in the initial state**. The **creation of the core hole in the photoemission process leads to an additional attractive potential for the valence level** of the impurity which **lowers it by an amount** U_{dc}.

The corresponding model Hamiltonian reads

$$H_{tot} = H_A + \epsilon_c n_c - U_{dc}(1 - n_c) \sum_\sigma n_{d\sigma} \ .$$

For the **spinless** SIAM this the famous **X-ray edge problem**.

The **model including spin** and **cannot be solved exactly for finite Coulomb interaction** U and various approximations were proposed. A treatment within the large degeneracy limit is discussed later.

Creation of the core hole: a quantum quench

As the ground state of the **combined system** has the form

$$\psi_c^\dagger|E_0(N)\rangle$$

with $|E_0(N)\rangle$ the ground state of the valence system with the core electron present, the **time development of the remaining pure valence** system **after removing the core electron** is described by the **modified Anderson Hamiltonian** $\tilde{H}_A$ with the energy ϵ_d of the impurity level replaced by $\epsilon_d - U_{dc}$. The creation of the core hole acts as a **quantum quench**.

The **core spectral function** is given by

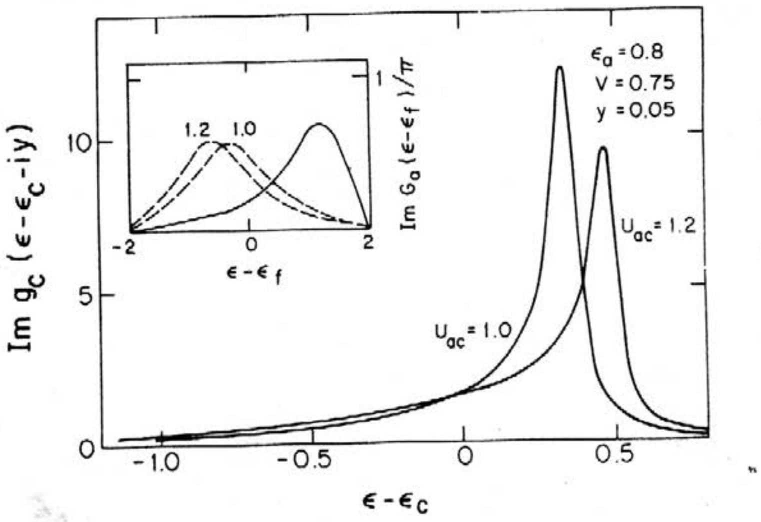
$$\rho_{cc}(\epsilon) = \langle E_0(N)|\delta(\epsilon - \epsilon_c - E_0(N) + \tilde{H}_A)|E_0(N)\rangle\ .$$

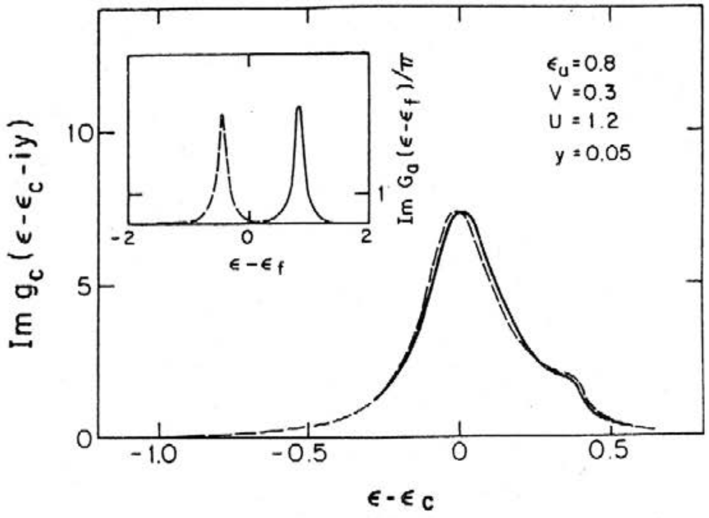
For the case of **noninteracting** valence electrons, i.e. $U = 0$ this problem falls into the class of the famous **X-ray edge singularity problem** (Nozières and de Dominicis, 1969). The sharp core level spectrum without the presence of the valence electrons is replaced by a continuum with a **power law singularity** at the **high energy edge**.

Core spectral function: “high energy” features

The core level spectrum can show **satellite peaks** corresponding to **higher energy eigenstates of** $\tilde{H}_A$ due to **physical processes that occur on a finite time scale** (M. Combescot and P. Nozières, 1971; A. Kotani and Y. Toyozawa, 1974; K. S. and O. Gunnarsson, 1977)

This has been addressed in detail e.g. for core levels of adsorbates at metal surfaces. For small coupling Γ a high energy resonance dominates the core level spectrum if the adsorbate level initially well above the chemical potential is pulled well below it when the core hole is created (spinless model).





(K.S., O. Gunnarsson, Solid State Comm. **18**, 691 (1977))

Infinite U SIAM with spin and orbital degeneracy

For an **f-orbital** the total degeneracy is $N_f = 14$ when spin-orbit and crystal-field splitting are neglected. Expressing V as

$$V = \frac{\tilde{V}}{\sqrt{N_f}}$$

with $\tilde{V}$ fixed, the model can be solved exactly in the limit $N_f \to \infty$ and for large but finite N_f a systematic approximation scheme can be set up at **zero temperature** : (O. Gunnarsson and K.S. (1982, 1983)):

At **finite temperatures** the "noncrossing approximation" (NCA) also uses $1/N_f$ as a small parameter.

- Y. Kuramoto, *Self-Consistent Perturbation Theory for the Dynamics of Valence Fluctuations* , Z.Phys. **B**, 37 (1983)
  (Earlier work: Keiter and Kimball (1970)): **no Wick's theorem**
- P. Coleman, *New approach to the mixed-valence problem*, Phys. Rev. **B**29, 3035 (1984)
  With the help of a **slave boson Wick's theorem can be used**

GS papers referred to in the following

- GS I: O. Gunnarsson and K.S., *Photoemission from Ce Compounds: Exact Model Calculation in the Limit of Large Degeneracy*, Phys. Rev. Lett. **50**, 604, (1982)

- GS II: O. Gunnarsson and K.S., *Electron spectroscopies for Ce compounds in the impurity model*, Phys. Rev. B**28**, 4315 (1983)

- GS III: O. Gunnarsson and K.S., *Double occupancy for the f orbital in the Anderson model for Ce compounds* , Phys. Rev. B**31**, 4815 (1985)

- GS IV: O. Gunnarsson and K.S., *Many body formulation of spectra of mixed valence systems* in "Handbook of the Physics and Chemistry of Rare Earths" Vol. 10, p.103-163, Elsevier (1987)

SIAM with large degeneracy

The N_f-fold degenerate single impurity Anderson Hamiltonian used in the following reads

$$H = \sum_{\nu=1}^{N_f} \left[\epsilon_f \psi_\nu^\dagger \psi_\nu + \int \epsilon \psi_{\nu\epsilon}^\dagger \psi_{\nu\epsilon} d\epsilon + \int \left[V(\epsilon) \psi_\nu^\dagger \psi_{\nu\epsilon} + H.c. \right] \right] + U \sum_{\nu<\mu} n_\nu n_\mu \ .$$

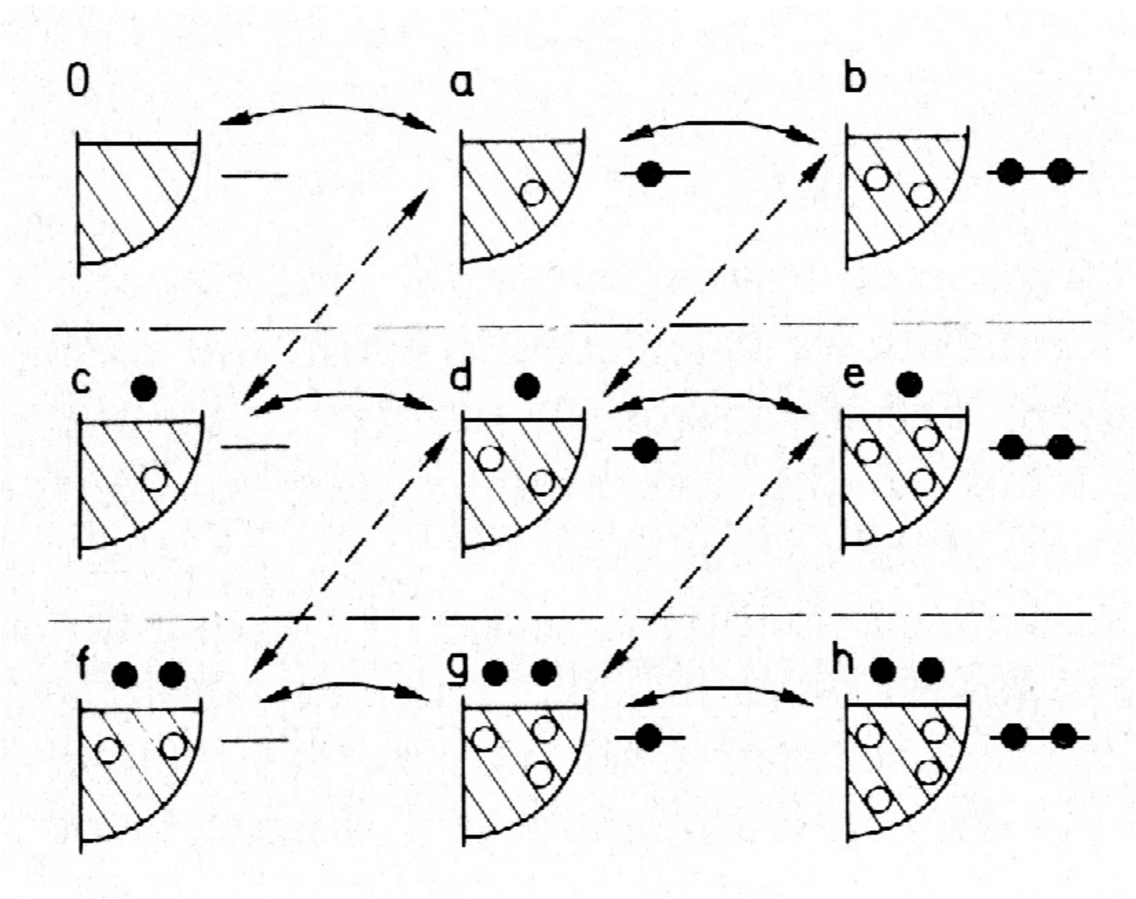
As $V(\epsilon)$ enters in the combinations $N_f V(\epsilon)^2$ and $V(\epsilon)^2$ it is useful to define

$$\tilde{V}(\epsilon) \equiv \sqrt{N_f} V(\epsilon)$$

and require that $\tilde{V}(\epsilon)$ is **independent of the degeneracy N_f**. This simplifies the discussion of the large degeneracy limit $N_f \to \infty$.

In the following the **ground state calculation** as well a the **"intermediate states method"** for the calculation of **spectra** is discussed in some detail. Already the **leading order analytical calculations** provide insight about the behaviour of the **Kondo resonance** in the large degeneracy limit.

Many-electron basis states for the ground state



Solid circles show **electrons** and *open circles* show *holes*.

The hatched part indicates the filled conduction bands and the horizontal lines the f-level. The **arrows show which states couple to each other**.

A **solid line** indicates the strength $\tilde{V}$ and a **dashed line** the strength $\tilde{V}/\sqrt{N_f}$.

In the **infinite** U case the **last column is missing**.

The **ground state calculation** is performed **variationally** using these many-electron basis states. We consider the **infinite U limit**.

In the state $|0\rangle$ all conduction states below the Fermi energy are filled and the f-level is empty. This state couples via H to the states "a". They are of the form

$$|\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum_{\nu} \psi^{\dagger}_{\nu} \psi_{\epsilon\nu}$$

in which a conduction electron has hopped into the f-level. They couple to states the "c"-states with a conduction electron-conduction hole pair

$$|E\epsilon\rangle = \frac{1}{\sqrt{N_f}} \sum_{\nu} \psi^{\dagger}_{E\nu} \psi_{\epsilon\nu} \ ,$$

where E refers to a conduction electron state **above** the Fermi level $(E > \epsilon_F)$, etc.

The **matrix elements coupling these states** are given by

$$\langle\epsilon|H|0\rangle = \tilde{V}(\epsilon) \ , \qquad \langle E\epsilon|H|\epsilon'\rangle = \tilde{V}(E)/\sqrt{N_f}\,\delta(\epsilon - \epsilon') \ .$$

As $\langle E\epsilon|H|\epsilon'\rangle \sim 1/\sqrt{N_f}$ **the ground state for $U = \infty$ to lowest order in** $1/N_f$ reads

$$|E_0\rangle^{(0)} = A\left[|0\rangle + \int_{-B}^{0} d\epsilon a(\epsilon)|\epsilon\rangle\right] .$$

For the corresponding ground state energy $E_0^{(0)}$ difference $\Delta E_0 \equiv E_0^{(0)} - \langle 0|H|0\rangle$ is **finite also in the thermodynamic limit**.

Using the coupling matrix element $\langle\epsilon|H|0\rangle = \tilde{V}(\epsilon)$ the Schrödinger equation leads to

$$\Delta E_0 = \int_{-B}^{0} \tilde{V}(\epsilon)a(\epsilon)d\epsilon, \qquad (\Delta E_0 - \epsilon_f + \epsilon)a(\epsilon) = \tilde{V}(\epsilon) .$$

Therefore ΔE_0 obeys the implicit equation

$$\Delta E_0 = -\int_{-B}^{0} \frac{\tilde{V}(\epsilon)^2}{\epsilon_f - \Delta E_0 - \epsilon} d\epsilon \equiv -\tilde{\Gamma}(\epsilon_f - \Delta E_0) \;\rightarrow\; \tilde{V}^2 \ln\frac{\epsilon_f - \Delta E_0}{\epsilon_f - \Delta E_0 + B} ,$$

where the energy integration was performed for an **energy independent** $\tilde{V}$. Defining the (positive) $\delta \equiv \epsilon_f - \Delta E_0$, $\tilde{\Delta} \equiv \pi\tilde{V}^2$, and $\tilde{\epsilon}_f \equiv \epsilon_f + (\tilde{\Delta}/\pi)\ln(\pi B/\tilde{\Delta})$ the equation for δ simplifies in the **“Kondo-limit” limit** $-\tilde{\epsilon}_f \gg \tilde{\Delta}$

$$\delta = (\tilde{\Delta}/\pi)e^{\pi(\tilde{\epsilon}_f - \delta)/\tilde{\Delta}} \quad \rightarrow \quad \boldsymbol{\delta \approx (\tilde{\Delta}/\pi)e^{\pi\tilde{\epsilon}_f/\tilde{\Delta}}} .$$

The coefficient $a(\epsilon)$ which determines the hole distribution is given by

$$a(\epsilon)^2 = (\tilde{\Delta}/\pi)/(\epsilon - \delta)^2 \ .$$

It grows on the energy scale δ as the Fermi energy is approched from below.

The total f-occupancy is determined by $\int a(\epsilon)^2 d\epsilon$. For the case of an energy independent $\tilde{V}$ one obtains $n_f = \tilde{\Delta}/(\tilde{\Delta} + \pi\delta)$.

In the Kondo limit the energy scale δ depends **exponentially** on $\pi\tilde{\epsilon}_f/\tilde{\Delta}$, which suggests that it can be, apart from a factor given by the Boltzmann constant k_B, interpreted as the **Kondo temperature:** $T_K = k_B\delta$. This will be further examined by calcualting the **one-particle Green's function** to leading order in $1/N_f$.

The infinite U lowest order calculation presented above can be extended to the case when the **spin-orbit splitting** $\Delta\epsilon_f$ is taken into account. The single f-level (with $N_f = 14$) is replaced by two levels (with $N_{f_1} = 6$ and $N_{f_2} = 8$ for $j = 5/2$ and $j = 7/2$) at ϵ_f and $\epsilon_f + \Delta\epsilon_f$. For the descrption of high-resolution experimental spectra of Ce compounds it is important to include the spin-orbit splitting.

Numerically performed ground state calculations of higher order in $1/N_f$ using the states in the figure **quickly converge** for $N_f = 14$.

The “intermediate state method” for spectra

The **theoretical description of photoemission** simplifies considerably when the emitted electron is assumed to have no interaction with the remaining $(N-1)$-electron system. In this **“sudden approximation”** the **photoemmision current** is **directly related to the spectral functions of one-particle Green’s functions** (see e.g. GS IV).

As shown the **zero temperature** local one-particle Green’s functions $G^<$ and $G^>$ can be expressed as an expectation value of the **resolvent of the many body Hamiltonian** H. One obtains the well known **Lehmann representation** by inserting the complete set of $(N \mp 1)$-electron **eigenstates of** H. For $G^<$ one can alternatively use the resolution of unity made of an **arbitrary complete set** $\{|i\rangle\}$ **of** $(N-1)$**-electron basis states**

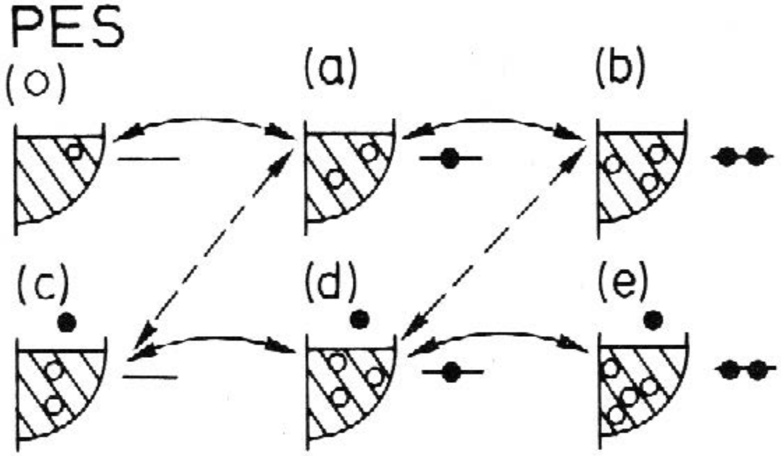
$$G^<_{\nu\nu}(z) = \sum_{ij} \langle E_0(N)|\psi^\dagger_\nu|i\rangle\langle i|(z+H-E_0(N))^{-1}|j\rangle\langle j|\psi_\nu|E_0(N)\rangle \ .$$

The inversion of the matrix $\tilde{H}(z)_{ij} \equiv \langle i|(z + H - E_0(N))|j\rangle$ would lead to the **exact result** for $G^<_{\nu\nu}(z)$

$$G^<_{\nu\nu}(z) = \sum_{ij} \langle E_0(N)|\psi^\dagger_\nu|i\rangle(\tilde{H}(z)^{-1})_{ij}\langle j|\psi_\nu|E_0(N)\rangle$$

if the procedure could be actually carried out for a **complete set of states**.

Approximations can be obtained by **truncating** the set $\{|i\rangle\}$ of **intermediate states** (GS). Useful results can be obtained again using a **classification of the states according to their contribution in orders of $1/N_f$**.



Valence photoemission spectrum to leading order in $1/N_f$

We consider the $U = \infty$ **case and work to lowest order in** $1/N_f$, for which the corresponding ground state was discussed. This yields

$$\psi_\nu |E_0\rangle^{(0)} = \frac{A}{\sqrt{N_f}} \int d\epsilon' a(\epsilon') \psi_{\epsilon'\nu} |0\rangle \ .$$

The (intermediate) basis states

$$|\epsilon'\nu\rangle \equiv \psi_{\epsilon'\nu}|0\rangle, \quad |\epsilon, \epsilon'\nu\rangle \equiv \frac{1}{\sqrt{N_f}} \sum_{\nu'} \psi^\dagger_{\nu'} \psi_{\epsilon\nu'} \psi_{\epsilon'\nu} |0\rangle$$

couple to **leading order** in $1/\sqrt{N_f}$ as

$$\langle \epsilon'\nu | H | \epsilon, \epsilon''\nu\rangle = \tilde{V}(\epsilon) \delta(\epsilon' - \epsilon'') \ .$$

Therefore for each **fixed value of** ϵ' the leading order calculation of the **many-body resolvent** is mathematically equivalent to a **“Friedrichs problem”** of coupling a “localized” level (here $|\epsilon'\nu\rangle$) to a continuum (here $|\epsilon, \epsilon'\nu\rangle$ with $-B \leq \epsilon \leq 0$).

This leads to

$$G^{<}_{\nu\nu}(z) = \frac{A^2}{N_f} \int_{-B}^{0} a(\epsilon')^2 \tilde{g}(z - \Delta E_0 + \epsilon_f - \epsilon') d\epsilon'$$

where

$$\tilde{g}(z) = \frac{1}{z - \epsilon_f - \tilde{\Gamma}(z)}, \quad \text{with} \quad \tilde{\Gamma}(z) = \int_{-B}^{0} \frac{\tilde{V}(\epsilon)^2}{z - \epsilon} d\epsilon \ .$$

In addition to a continuum part for $-B \le \epsilon \le 0$ the function $\tilde{g}(z)$ has **pole** at $z = \delta = \epsilon_f - \Delta E_0$ as the ground state energy is obtained from

$$\Delta E_0 = -\tilde{\Gamma}(\delta).$$

The pole has the strength $(1 - d\tilde{\Gamma}/dz)^{-1}|_\delta = 1 - n_f$.

The **total f spectral function** $\rho^{<}_{f}(\epsilon) \equiv \sum_\nu \mathrm{Im} G^{<}_{\nu\nu}(\epsilon - i0)/\pi$ therefore has the **pole contribution**

$$\rho_f^<(\epsilon) = \frac{(1-n_f)^2\tilde{V}(\epsilon)^2}{(\delta-\epsilon)^2}, \quad \text{for} \quad -\delta \leq \epsilon \leq 0 \ .$$

This **“low energy” spectral weight** rises sharply as ϵ approaches $\epsilon_F = 0$ from below. It is the **tail of the Kondo resonance** present at $\epsilon \approx \delta$ in the spectral function $\rho_f^>(\epsilon)$ describing **inverse** photoemission (BIS), discussed in the following.

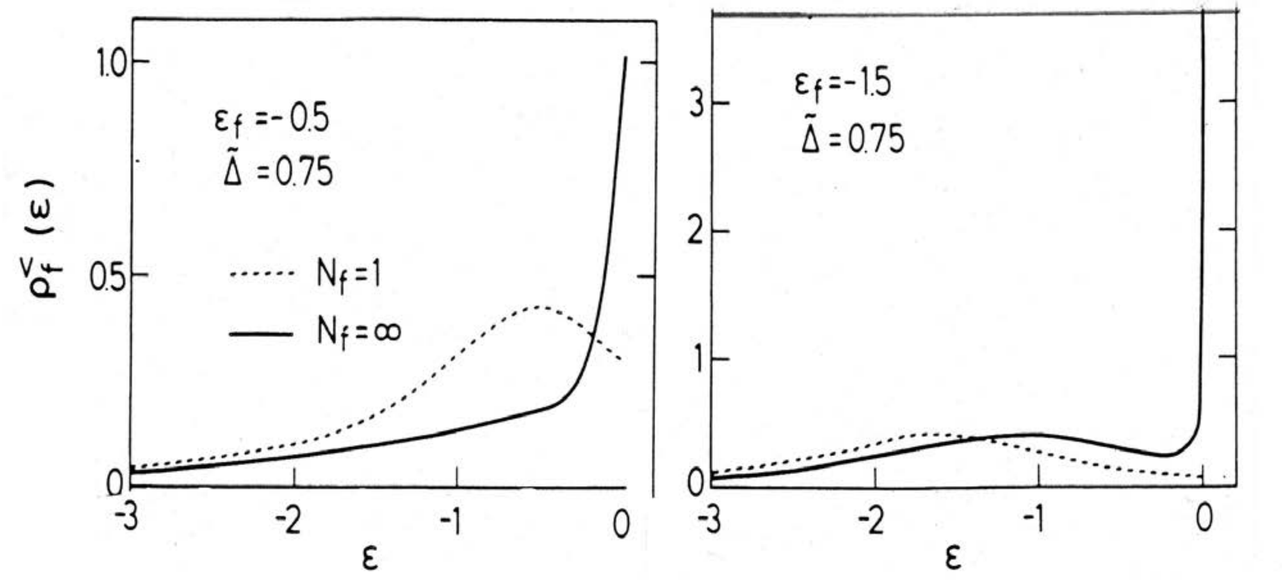
The **total weight** of $\rho_f^<$ from the pole contribution is given by $n_f(1-n_f)$. It becomes **very small in the Kondo limit $n_f \approx 1$.** Then most of the spectral weight (for $-\epsilon \gg \delta$) is well approximated by

$$\rho_f^<(\epsilon) \approx \mathrm{Im}\tilde{g}(\epsilon - i0)/\pi \ .$$

The **“ionization peak”** near ϵ_f **dominates the spectrum**.

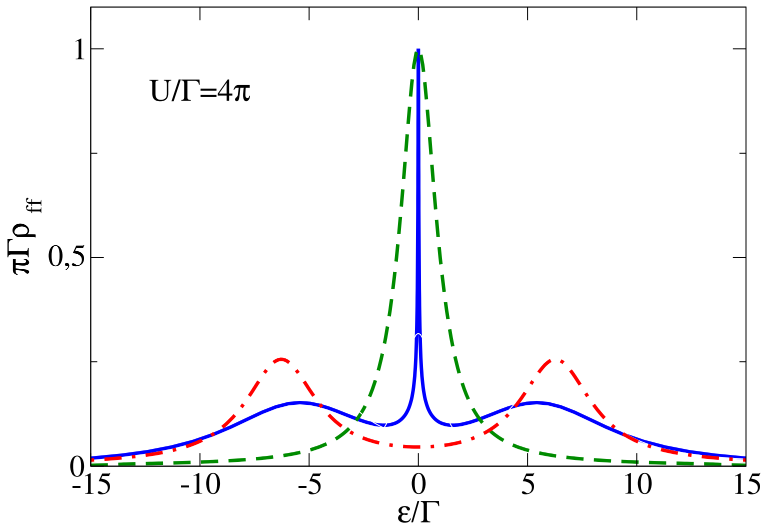
Its **width** is given by $N_f\Delta = \tilde{\Delta}$:

there are N_f channels to fill the empty f-level.



Comparison of the leading order result for $\rho_f^<(\epsilon)$ (full lines) with the “broadened atomic limit” approximation $\rho_f^<(\epsilon) \approx \tilde{g}(\epsilon - i0)/\pi$.

Compare the $\epsilon_f = -1.5$ figure to the $\epsilon < 0$ part of

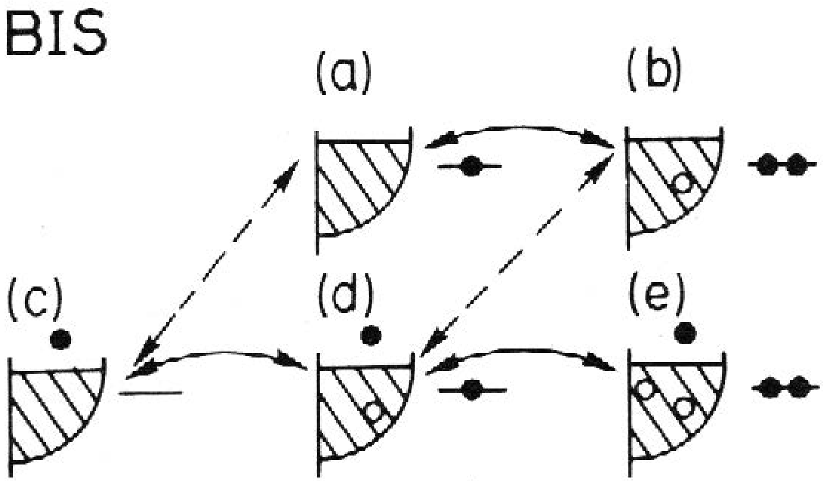


Inverse photoemission (BIS)

In inverse photoemission, earlier called **Bremsstrahlung isochromat spectroscopy (BIS)**, the sample is bombarded by electrons which make radiative transitions into lower-lying $(N+1)$-electron states. Here we discuss transitions into the f-level. The theoretical description is in terms of

$$G^{>}_{\nu\nu}(z) = \langle E_0(N)|\psi_\nu \frac{1}{z - H + E_0(N)} \psi^\dagger_\nu |E_0(N)\rangle \ .$$

The **intermediate basis states** are



As the integrated weight of the total spectral function $\rho_{\nu\nu} = \rho^<_{\nu\nu} + \rho^>_{\nu\nu}$ is unity and $\int \rho^<_{\nu\nu}(\epsilon) d\epsilon = n_f/N_f$ holds, with $n_f \le 1$ in the infinite U case, the **integrated weight of $\rho^>_{\nu\nu}$** is given by $1 - n_f/N_f$, i.e. it is **larger by a factor N_f** than the **integrated weight of $\rho^<_{\nu\nu}$**.

In order to fulfill $\rho^<_{\nu\nu}(0) = \rho^>_{\nu\nu}(0)$ expected for an exact description at any finite N_f requires to **treat $G^>_{\nu\nu}$ differently** from the of calculation $G^<_{\nu\nu}$.

As the **leading order ground state** is used one has to calculate the expectation value of the resolvent of the many body Hamiltonian with

$$\psi^\dagger_\nu |E_0\rangle^{(0)} = A \left[\psi^\dagger_\nu |0\rangle + \frac{1}{\sqrt{N_f}} \sum_{\nu'(\neq\nu)} \int d\epsilon a(\epsilon) \psi^\dagger_\nu \psi^\dagger_{\nu'} \psi_{\epsilon\nu'} |0\rangle \right] .$$

In the **first state** on the rhs the f-level is **singly occupied (“f^1”)** while in the **second term** it is **doubly occupied (“f^2”)**.

In a first attempt one would take the states on the rhs as the intermediate states to calculate $G^>_{\nu\nu}$. If one **focusses on the f^1-peak in the $U \to \infty$ limit**, only the state $|\nu\rangle = \psi^\dagger_\nu |0\rangle$ plays a role and one obtains

$$G^{>}_{\nu\nu}(z) \approx \frac{1-n_f}{z+\Delta E_0-\epsilon_f} = \frac{1-n_f}{z-\delta} \ .$$

The corresponding peak has zero width and in the Kondo limit the small weight $1-n_f \ll 1$. In order to fullfill $\rho^{<}_{\nu\nu}(0) = \rho^{>}_{\nu\nu}(0)$ one has to go **one order higher in $1/N_f$**, i.e to include the states c) and d) in the infinite U limit. This leads to

$$G^{>}_{\nu\nu}(z) = \frac{1-n_f}{z+\Delta E_0-\epsilon_f-\mu(z)},$$

with

$$\mu(z) = \int_0^B \frac{V(E)^2}{z+\Delta E_0-E+\tilde{\Gamma}(-z-\Delta E_0+E+\epsilon_f)} dE \ .$$

In the **Kondo limit** this leads to

$$\rho^{>}_{f}(\epsilon) = \frac{(1-n_f)^2\tilde{V}(\epsilon)^2}{(\epsilon-\delta-\mathrm{Re}\mu(\epsilon))^2+((1-n_f)\pi V(\epsilon))^2}, \quad \text{for} \quad 0 \le \epsilon \le \delta$$

Now the **Kondo peak has a half width** $(1-n_f)\pi V(\delta)^2 \approx \pi\delta/N_f$ and in a strict $1/N_f$ expansion $\rho^{>}_{f}(\epsilon)$ **joins smoothly to the presented low energy result for** $\rho^{<}_{f}(\epsilon)$.

Let us **summarize** the behaviour of the total spectral function $\rho_f = \rho_f^< + \rho_f^>$ in the **Kondo regime** $-\epsilon_f \gg \tilde{\Delta}$ for large values of U:

The **ionization peak** near ϵ_f has the weight $n_f \approx 1$.

The weight of the f^1 **Kondo peak** slightly above ϵ_F is $(1 - n_f)N_f$, and the f^2 peak near $\epsilon_f + U$ has a weight $n_f(N_f - 1) \approx N_f - 1$.

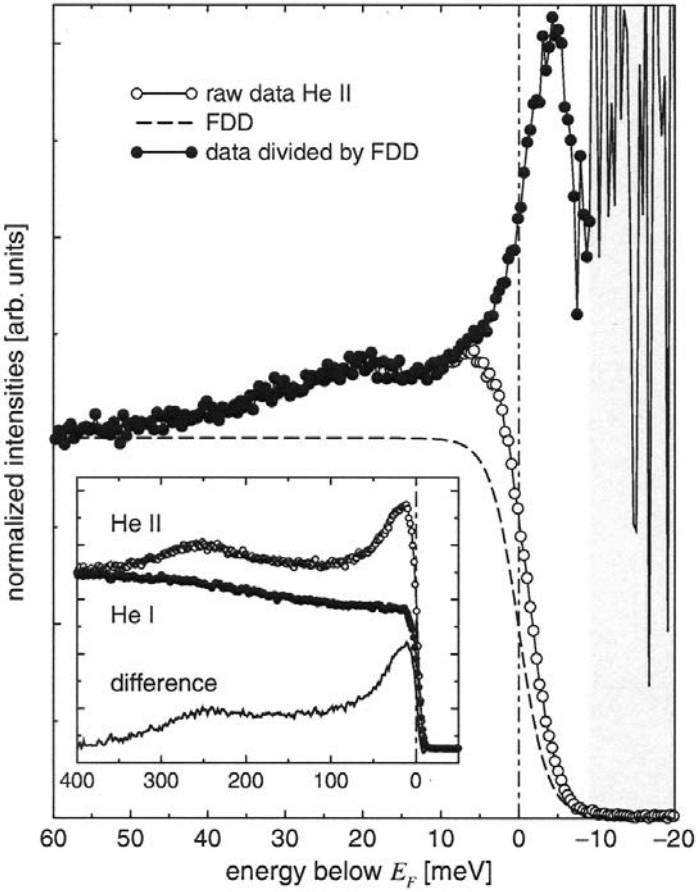
Therfore even for $n_f = 0.9$ and $N_f = 14$ the **weight of the Kondo peak** is **higher** than the **weight of the ionization peak**:

Despite the fact that that there is a small chance, $1 - n_f$, to find the f-level empty, there are N_f different ways to put the electron.

The weight of the Kondo peak in the BIS specrum is a factor N_f larger than the part seen in photoemission.

Photoemission spectrum of $\mathrm{CeCu_2Si_2}$: Reinert et al. PRL 87, 106401 (2001)

$T = 11\mathrm{K}$:



$$\rho_{ff}(\epsilon) = \frac{\rho^{<}_{ff}(\epsilon)}{f(\epsilon)}$$

Spectra involving core holes

Core level XPS and X-ray absorption spectroscopy provide **additional information about the valence electrons**. In the XPS-case the core spectral function is given by

$$\rho_c(\epsilon) = \langle E_0(N)|\delta(\epsilon - \epsilon_c - E_0(N) + \tilde{H})|E_0(N)\rangle \ ,$$

where in $\tilde{H}$ the f-level has the energy $\epsilon_f - U_{fc}$.

In the **infinite** U case to order $(1/N_f)^0$ the ground state is expressed in terms of the states $|0\rangle$ and $|\epsilon\rangle$. They are also used as **intermediate states in the leading order calculation of** $G_{cc}^< = G_{cc}$. This is again a **"Friedrichs problem"** and the $00, 0\epsilon, \epsilon 0$ and $\epsilon\epsilon'$ matrix elements of the corresponding resolvent are all needed. The straightforward calculation yields

$$\rho_c(\epsilon + \epsilon_c) = (1 - n_f)\left(\frac{U_{fc}}{\epsilon - U_{fc}}\right)^2 \tilde{\rho}_f(\epsilon - \Delta E_0 + \epsilon_f - U_{fc}) \ ,$$

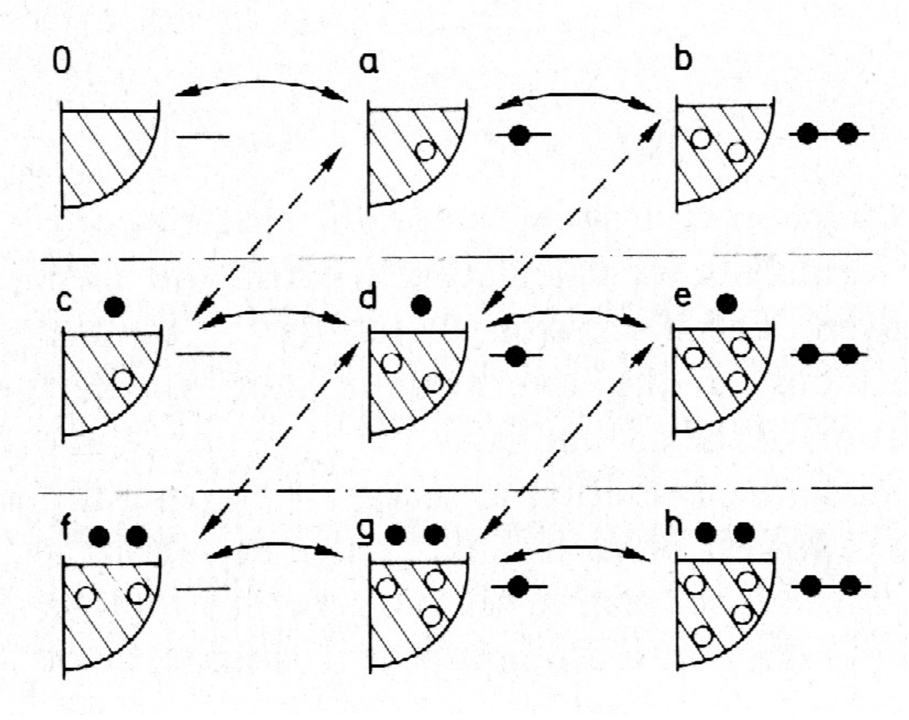
where

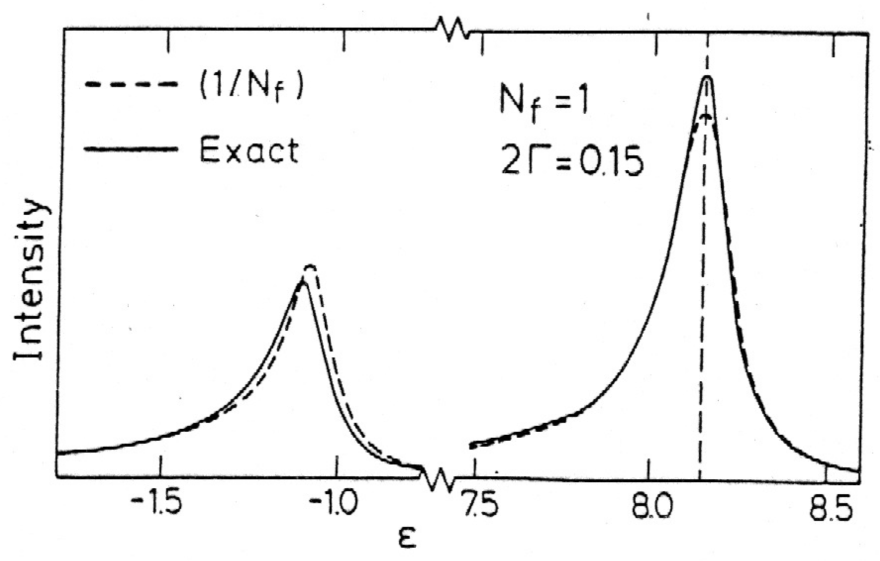
$$\tilde{\rho}_f(\epsilon) = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\epsilon + i0 - \epsilon_f + U_{fc} - \tilde{\Gamma}(\epsilon + i0)} \ .$$

In this leading order approximation the core spectrum is directly related to the **"valence spectrum"** $\tilde{\rho}_f$. This clearly shows that **core level spectroscopy gives information about properties of the valence electrons**, like n_f, ϵ_f and Δ.

To **test the accuracy** of the $1/N_f$ method one can study the **limit** $N_f = 1$, where the exact solution can be obtained by solving the Nozierès-de Dominicis integral equation numerically.

A comparison of the $1/N_f$ result including the state 0, a, c, and d is shown on the next page





The **exact result** has an **infrared singularity at threshold** which is **not** present in the $1/N_f$ calculation. This is not very prominent in the figure as a Lorentzian "life time" broadening was introduced.

X-ray absorption spectroscopy of $3d \to 4f$ transitions has **formal similarities with inverse photoemission** , as an electron is added to the f-level. The difference is that the **final state has the core hole present**. The theoretical description therefore, as in core-hole XPS, has to use the **Hamiltonian** $\tilde{H}$.

Comparison with experimental spectra

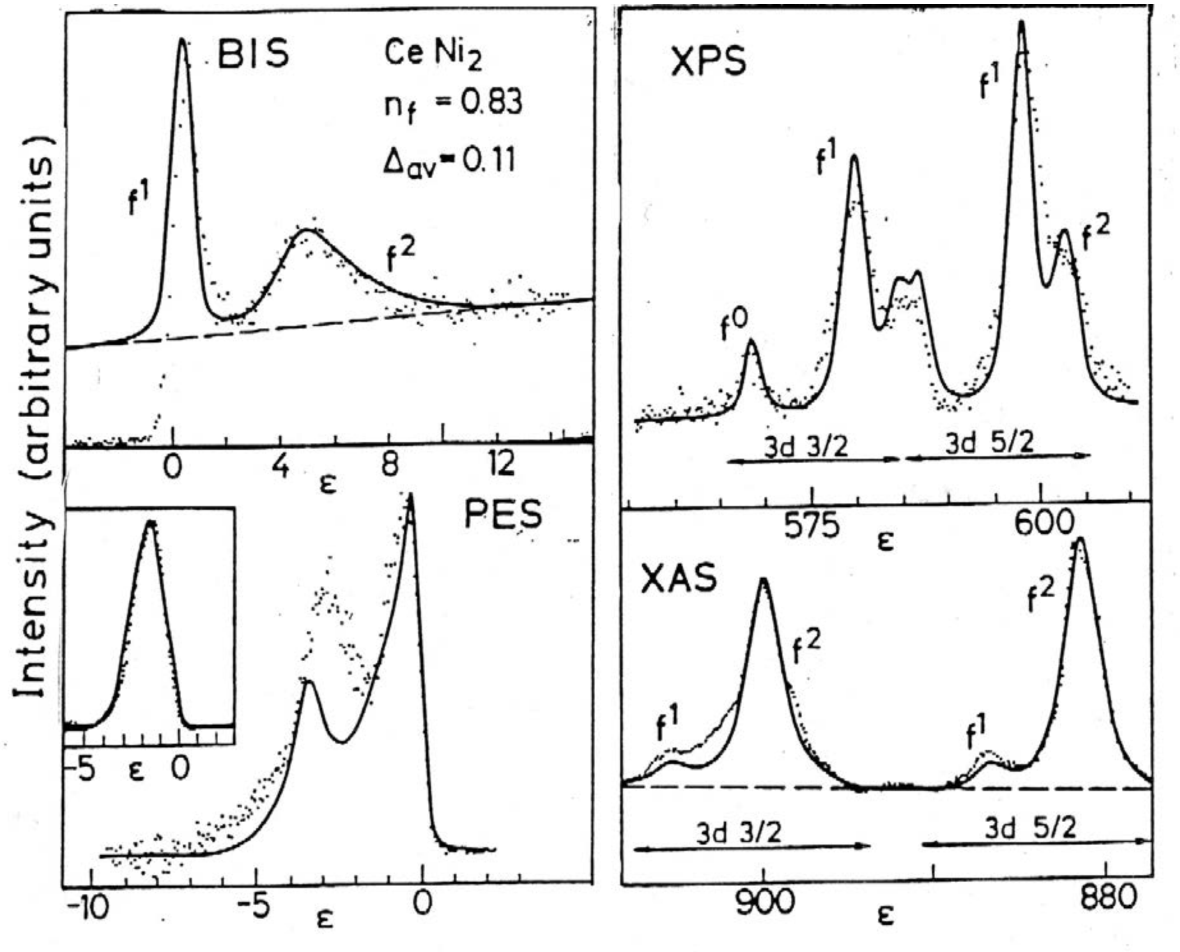
The model calculations for spectra using the **impurity model** are used frequently for a **comparison with experimental data** of lanthanide materials.

An example for systems with essentially zero f-occupancy in the ground state are La compounds. In Ce systems the f^0 and f^1 configurations play the important role.

Even in dense systems spectra calaculated by the intermediate states method for the Anderson impurity model are often in good agreement with experiment (see e.g. GS IV).

Using **different spectroscopies** a **part of the data** may suffice to **determine the model parameters** by fitting to the peak positions and their widths. Then the additional data can be used as a **consistency check** or for **predicting results of further measurements**.

$CeNi_2$ **spectra :**



(J. Allen et al. Advances in Physics **35**, 37 (1986))

The **two components** of the XAS (and XPS) spectrum in the figure are due to transitions from the **spin-orbit split** $3d\ 3/2$ **and** $3d\ 5/2$ **levels**.

Here an **incomplete list of “later” papers** related to the issues presented here:

- H.O. Frota and L.N. Olivera, *Photoemission spectroscopy for the spin-degenerate Anderson model* Phys. Rev. B**46**, 15207 (1986)
- for a review see: R. Bulla, T.A. Costi, and T. Pruschke, *Numerical renormalization group for quantum impurity systems*, Rev. Mod. Phys. **80**, 395 (2008)
- N.E. Bickers, *Review of techniques in the large-N expansion for dilute magnetic alloys*, Rev. Mod. Phys. **59**, 845 (1987)
- J. Holm and K. Schönhammer, *Generalized slave-boson treatment of double occupany of the f-orbital in the single impurity Anderson model*, Solid State Commun. **69**, 969 (1989)
- T. Pruschke and T. Grewe, *The Anderson model with finite Coulomb repulsion*, Z. Phys. **74**, 439 (1989)
- H. Haule, S. Kirchner, J. Kroha, and P. Wölfle, *Anderson impurity model at finite interaction U: Generalized noncrossing approximation*, Phys. Rev. B**64**, 155111 (2001)
- M.R. Galpin, A.B. Gilbert, and D.E. Logan, *A local moment approach to the degenerate Anderson model*, J. Phys. Condes. Matter **21**, 375602 (2009)

Outlook

There were many theoretical developments in the last thirty years which go beyond the $1/N_f$ method presented here in some detail. The intermediate states method nevertheless has remained a **valuable tool in the hands of experimentalists**.

Presently a hot subject is to find **controlled approximations** for the fate of the **Kondo resonance** in systems **far from equilibrium** (like quantum dots).

When I was a postdoc with H. Suhl at UCSD in 1975/76 we often talked about the open problems in Kondo physics (at the time in connection with adsorbates).

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He used to say

“Like South America the Kondo problem will always have a great future”