Electronic Structure Calculations with Dynamical Mean Field Theory

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DFT considers total energy \( E \) as a functional of the density \( \rho \) and reduces the problem to solving single particle Kohn Sham equations with energy independent potential:

\[
(-\nabla^2 + V_{DFT}) \psi_k = \varepsilon_k \psi_k
\]

From here various properties can be deduced with spectacular accuracies:

**Band structures** \( \varepsilon_k \)
- Single particle spectra
- Densities of states
- Photoemission & Optics
- Transport & Superconductivity

**Density** \( \rho \)
- Magnetic Moments
- Bonding & Covalency
- Static Respone Functions

**Energy** \( E \)
- Crystal structures
- Equations of State
- Phonon and Magnon Spectra

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**Electronic Structure**
Problems with Strongly Correlated Systems

Density functional calculations using local density approximation (LDA) grossly fail for materials with strong correlations:

- Ground state volume of $\delta$-Pu is 30% too small within LDA.
- Multiplet transitions seen in many lanthanides and actinides cannot be resolved by DFT-LDA calculation.
- Kondo and mixed valence physics is missing.
- Mott physics, paramagnetic insulating behavior cannot be modeled by DFT.
Mott Transition is not here!

Paramagnetic Mott insulators at high temperatures cannot be understood based on standard band theory argument.

According to the band theory a material with partially filled band will remain metallic at all interatomic distances $E_f$.

Atomic limit is not correctly described.
Excitations in Atoms

\[ E_n = \varepsilon_d n + \frac{1}{2} U(n-1) \]

\[ E_{n-1} = \varepsilon_d (n-1) + \frac{1}{2} U(n-1)(n-2) \]

\[ E_{n+1} = \varepsilon_d (n+1) + \frac{1}{2} U(n+1)n \]

Electron Removal Spectrum

\[ E_n - E_{n-1} = \varepsilon_d + Un - U / 2 \]

Electron Addition Spectrum

\[ E_n - E_{n+1} = \varepsilon_d + Un + U / 2 \]
Atomic Self-Energies have singularities

Ground state energies for configurations \(d^n, d^{n+1}, d^{n-1}\) give rise to electron removal \(E_n - E_{n-1}\) and electron addition \(E_n - E_{n+1}\) spectra. Atoms are always insulators!

\[
E_n - E_{n-1} = \tilde{\epsilon}_d - U/2
\]

Electron removal

\[
E_n - E_{n+1} = \tilde{\epsilon}_d + U/2
\]

Electron addition

or two poles in one-electron Green function

\[
G(\omega) = \frac{1/2}{\omega - \tilde{\epsilon}_d + U/2} + \frac{1/2}{\omega - \tilde{\epsilon}_d - U/2}
\]

Coulomb gap

Self-energy with a pole is required:

\[
G(\omega) = \frac{1}{\omega - \tilde{\epsilon}_d - \Sigma(\omega)} = \frac{1}{\omega - \tilde{\epsilon}_d - \frac{U^2}{4(\omega - \tilde{\epsilon}_d)}}
\]

This is missing in DFT effective potential or LDA+U orbital dependent potential
Mott Insulators as Systems near Atomic Limit

Classical systems: MnO ($d^5$), FeO ($d^6$), CoO ($d^7$), NiO ($d^8$).

Neel temperatures 100-500K. Remain insulating both below and above $T_N$.

**LDA/ LDA+U**, other static mean field theories, cannot access paramagnetic insulating state.

$$G_{LDA}(\omega) = \frac{1}{\omega - \varepsilon_d - V_{LDA}}$$

Frequency dependence in self-energy is required:

$$G_{Hubbard}(\omega) = \frac{1}{\omega - \varepsilon(k) - \Sigma_d(\omega)} = \frac{1}{\omega - \varepsilon(k) - \frac{U^2}{4(\omega - \varepsilon_d)}}$$

$$= \frac{1/2}{\omega - \varepsilon(k) + U/2} + \frac{1/2}{\omega - \varepsilon(k) - U/2}$$

Sometimes bringing spin dependence helps however!
Properties of UO$_2$ & PuO$_2$

- Both are Mott-Hubbard insulators, $E_g \approx 2$ eV.
- UO$_2$ is AFM with $T_N = 30$K, while PuO$_2$ is non-magnetic.
Ground states for f-electrons

j = 7/2

~1 eV

j = 5/2

~0.1 eV

$\Gamma_1(1)$

$\Gamma_4(3)$

$\Gamma_3(2)$

$\Gamma_5(3)$

$\Gamma_7(2\ \text{fold})$

$\Gamma_8(4\ \text{fold})$

$\Gamma_6(2\ \text{fold})$

$\Gamma_7(2\ \text{fold})$

$\Gamma_8(4\ \text{fold})$

$\Gamma_6(2\ \text{fold})$

$\Gamma_7(2\ \text{fold})$

$\Gamma_8(4\ \text{fold})$

$\Gamma_5(3)$

$\Gamma_3(2)$

$\Gamma_4(3)$

$\Gamma_1(1)$

$\Gamma_6(2\ \text{fold})$

$\Gamma_7(2\ \text{fold})$

$\Gamma_8(4\ \text{fold})$

$\Gamma_1(1)$

$\Gamma_4(3)$

$\Gamma_3(2)$

$\Gamma_5(3)$
**Localized electrons: Dynamical Mean Field Approach**

Electronic structure is found by solving Dyson equation

\[
[-\nabla^2 + \Sigma(\omega)]\psi_k(r, \omega) = \epsilon_k(\omega)\psi_k(r, \omega)
\]

where dynamical self-energy for f-electrons is extracted by solving Anderson impurity model

\[
\hat{\Sigma}_f(\omega) = \omega - \epsilon_f - [\hat{G}_{imp}(\omega)]^{-1} - \sum_k \frac{V_{kf}^2}{\omega - \epsilon_k}
\]

Poles of the Green function \( G(k, \omega) = \frac{1}{\omega - \epsilon_k(\omega)} \)

describe atomic multiplets, Kondo resonances, Zhang-Rice singlets, etc.

Better description compared to DFT-LDA is obtained
Strongly Correlated Materials

Not well described by a “standard model” based on band theories: Fermi liquid theory, Kohn Sham DFT, GW, where QPs are a reference system.
Density is not a good variable to describe total energies of strongly correlated systems.

Formulate a functional where electronic spectral function is a variable. This will predict both energetics and spectra.

A functional where local spectral function $N(E)$ is at the center of interest is based on Dynamical Mean Field Theory.

Can be entitled as Spectral Density Functional

(Kotliar, SS, Haule, Udovenko, Parcolett, Marianetti, Reviews of Modern Physics, 2006)
**Green Function Theory**

Effective action formulation (Chitra, Kotliar, PRB 2001) \( x = (r, \tau) \)

\[
S = \int dx \psi^+(x) [\partial_\tau - \nabla^2 + V_{\text{ext}}(x)] \psi(x) + \\
\int dx dx' \psi^+(x) \psi^+(x') v_C(x - x') \psi(x) \psi(x')
\]

- Adding an auxiliary source field to the system \( J(x, x') \) to probe Green function
  \[
  S[J] = S + \int dx dx' J(x, x') \psi(x') \psi^+(x)
  \]
  \[
  W[J] = -\ln \int D[\psi^+ \psi] \exp(-S'[J])
  \]

- Eliminate source in favor of conjugate field using Legendre transform, obtain **Free Energy Baym-Kadanoff Functional**
  \[
  \Gamma_{BK}[G] = W[J] - Tr[JG]
  \]
Freedom to construct functionals

Choosing various source fields, various functionals can be obtained:

Example 1. Static local source $J(x) = J(r) \delta(\tau)$

$$S[J] = S + \int dr J(r) \psi(r) \psi^+(r)$$

probes the density => **Density Functional** $\Gamma_{DFT}[\rho]$ is obtained.

Example 2,3,4… Choose appropriate source – obtain TD-DFT, Spin Polarized DFT, LDA+U, …

In all cases free energy of the system is accessed in extremum. 
(Kotliar, Savrasov, in New Theoretical Approaches to Strongly Correlated Systems, 2001)
Spectral Density Functional Theory is obtained using local source

\[ J_{\text{loc}}(x, x') = J(x, x')\theta(r, r') \]

which probes local Green function

\[ G_{\text{loc}}(r, r', i\omega) = G(r, r', i\omega)\theta(r, r') \]

Total Free Energy is accessed

\[ \Gamma_{\text{SDF}}[G_{\text{loc}}] = 0 \]

\[ \frac{\delta \Gamma_{\text{SDF}}}{\delta G_{\text{loc}}} = 0 \]
Local Green function Functionals

$$\rho(r) = \sum_{i\omega} G(r, r, i\omega)e^{i\omega q^*} = \sum_{i\omega} G_{DFT}(r, r, i\omega)e^{i\omega q^*}$$

Family of Functionals

$$\Gamma_{BK}[G(r, r', i\omega)] \quad \Gamma[G_{loc}(r, r', i\omega)] \quad \Gamma_{DFT}[\sum_{i\omega} G(r, r, i\omega)e^{i\omega q^*}]$$

$$r \rightarrow r'$$

$$
\Gamma_{DFT}[\rho(r)] \\
G_{loc}(r, r', i\omega) = G(r, r', i\omega)\theta(r, r')
$$
Kinetic energy & generalization of Kohn-Sham Idea

To obtain kinetic functional:

\[ \Gamma_{SDF}[G_{loc}] = K_{SDF}[G_{loc}] + \Phi_{SDF}[G_{loc}] \]

introduce **fictitious** particles which describe local Green function:

\[ G(r \in \Omega_c, r', i\omega) = \sum_{kj} \frac{\psi_{kj}(r)\psi^*_{kj}(r')}{\omega - E_{kj}} \]

Exactly as in DFT:

\[ G_{KS}(r, r', \omega) = \sum_{kj} \frac{\psi_{kj}(r)\psi^*_{kj}(r')}{\omega - E_{kj}} \]

\[ K_{DFT}[\rho] \rightarrow K_{DFT}[G_{KS}] \]
Local Self-Energy of Spectral Density Functional

- Spectral Density Functional looks similar to DFT

\[ \Gamma[\psi_{kj\omega}] = \sum_{kj} \sum_{i\omega} f_{kj\omega} \varepsilon_{kj\omega} - \sum_{i\omega} \int \mathcal{M}_{\text{eff}}(r, r', i\omega) G(r, r', i\omega) dr dr' \]

\[ + \int \rho(r) V_{\text{ext}}(r) dr + E_H[\rho] + \Phi_{xc}[G_{\text{loc}}] \]

\[ f_{kj\omega} = \frac{1}{(i\omega + \mu - E_{kj\omega})} \]

- Effective mass operator is local by construction and plays auxiliary role exactly like Kohn-Sham potential in DFT

\[ \mathcal{M}_{\text{eff}}(r, r', \omega) = [V_{\text{ext}}(r) + V_H(r)] \delta(r - r') + \frac{\delta \Phi_{xc}}{\delta G_{\text{loc}}(r, r', \omega)} \]

- Energy dependent Kohn-Sham (Dyson) equations give rise to energy-dependent band structure

\[ -\nabla^2 \psi_{kj\omega}(r) + \int \mathcal{M}_{\text{eff}}(r, r', \omega) \psi_{kj\omega}(r') dr' = E_{kj\omega} \psi_{kj\omega}(r) \]

- \( E_{kj\omega} \) have physical meaning in contrast to Kohn-Sham spectra. They are designed to reproduce local spectral density.
Local Dynamical Mean Field Approximation

- Exchange-correlation functional $\Phi_{xc}[G_{loc}]$ is unknown

- **Local dynamical mean field approximation** for $\Phi_{xc}[G_{loc}]$

  Sum of diagrams constructed with local Green function $G_{loc}$ and bare Coulomb interaction $v_C$

- Remarkably, that sum can be performed by mapping onto auxiliary quantum impurity model subjected to self-consistency condition (Georges, Kotliar, 1991)

\[
S_{imp} = \int_{\Omega_{loc}} dx \psi^+(x) G_0^{-1}(x, x') \psi(x) + \int_{\Omega_{loc}} dx dx' \psi^+(x) \psi^+(x') v_C(x - x') \psi(x) \psi(x') \\
G_0^{-1}(x, x') = G_{loc}^{-1}(x, x') + M_{int}(x, x')
\]
Dynamically Screened Interaction

- Interaction functional in Baym-Kadanoff theory (Chitra, Kotliar, 2001)

\[ \Phi_{BK}[G] = E_H - \frac{1}{2} Tr \ln W + \frac{1}{2} Tr [\nu_C^{-1} - W^{-1}] W + \Psi_{BK}[G,W] \]

obtained via introducing another source coupled to \( \psi^+(x)\psi^+(x')\psi(x)\psi(x') \)

Functional \( \Gamma_{BK}[G,W] \) is extremized both over \( G \) and over \( W \)

\[ G = G_0 - G_0 \Sigma_{\text{int}} G \]
\[ W = \nu_C - \nu_C \Pi W \]

- Interaction functional in spectral density functional theory is obtained via introducing a local source which probes \( \psi^+(x)\psi^+(x')\psi(x)\psi(x') \) in part of the space:

\[ W_{loc}(r,r',\omega) = W(r,r',\omega) \theta(r,r') \]

May be a formal way to define on-site “U”
Local Interaction & “Kohn-Sham” interaction

- Do the same Kohn-Sham trick to find a “non-interacting” functional (Chitra, Kotliar, 2001) Introduce auxiliary interaction $\mathcal{W}(r, r', \omega)$

$$\mathcal{W}(r, r', \omega) = W(r, r', \omega) = W_{\text{loc}}(r, r', \omega), r \in \Omega, r' \in \Omega_{\text{loc}}$$

$$\mathcal{W}(r, r', \omega) \neq W(r, r', \omega), W_{\text{loc}}(r, r', \omega) = 0, r \in \Omega, r' \notin \Omega_{\text{loc}}$$

- Interaction Functional in Spectral Density Functional Theory

$$\Phi_{\text{SDF}}[G_{\text{loc}}, \mathcal{W}] = E_H - \frac{1}{2} \text{Tr} \ln \mathcal{W} + \frac{1}{2} \text{Tr}[v_C^{-1} - \mathcal{W}^{-1}]\mathcal{W} + \Psi_{\text{SDF}}[G_{\text{loc}}, \mathcal{W}]$$

Functional $\Gamma_{\text{BK}}[G, \mathcal{W}]$ is extremized both over $G$ and over $\mathcal{W}$

$$G = G_0 - G_0 M_{\text{int}} G$$

$$\mathcal{W} = v_C - v_C \mathcal{P} \mathcal{W}$$

- $\mathcal{P}$ is an auxiliary susceptibility (similar to mass operator $M$)$\mathcal{P}$ is manifestly local within $\Omega_{\text{loc}}$
Extended Dynamical Mean Field Theory

Reduction to impurity model \((Si, Kotliar, 1995, Chitra, Kotliar 2001)\)

\[
S_{imp} = \int_{\Omega_{loc}} dx \psi^+(x) G^{-1}_{0}(x, x') \psi(x) + \int_{\Omega_{loc}} dxdx' \psi^+(x) \psi^+(x') V_0(x - x') \psi(x) \psi(x')
\]

leads to definitions of bath Green function and bath interaction which is input to impurity model

\[
G^{-1}_0(x, x') = G^{-1}_{loc}(x, x') + M_{int}(x, x')
\]

\[
V^{-1}_0(x, x') = W^{-1}_{loc}(x, x') + P(x, x')
\]
Self-Consistency

Spectral Density Functional Theory within Local Dynamical Mean Field Approximation

\[ G^{-1} = \mathcal{M} - G_0^{-1} \]
\[ W^{-1} = \mathcal{P} - v_c^{-1} \]
\[ G_{loc} = G \theta_c \]
\[ W_{loc} = W \theta_c \]
\[ G_0^{-1} = G_{loc}^{-1} + \mathcal{M} \]
\[ v_0^{-1} = W_{loc}^{-1} + \mathcal{P} \]

Local Impurity Model

\[ M, \mathcal{P} \]
Further Approximations

- **LDA+DMFT method and its static limit: LDA+U**
  
  
  Why not think of LDA as most primitive impurity solver?
  Divide electrons onto light and heavy. Apply LDA for light electrons.
  Use more intelligent solution of impurity problem for heavy electrons.

- **Local GW approximation**
  
  (Kotliar+SS, 2001, Zein+Antropov 2002)
  
  Solves impurity model using GW diagram: \( M_{xc} = -G_{loc} W_{loc} \)

- **GW+DMFT Method**
  
  (George+Aryasetyavan+Bierman, 2002, Zein+SS+Kotliar, 2006)
  
  Eliminates problems of input “U” and double counting.
LDA+DMFT as natural extension of LDA+U

In LDA+U correction to the potential

$$\Delta V^\sigma_{LDA+U} = \Sigma^\sigma_{atomic}(\omega \rightarrow \infty) - V_{DC} = \Sigma^\sigma_{atomic, HF} - V_{DC}$$

is just the Hartree-Fock value of the exact atomic self energy.

Why don’t use exact atomic self-energy itself instead of its Hartree-Fock value? This is so called Hubbard I approximation to the electronic self-energy.

Next step: use self-energy from atom allowing to hybridize with conduction bath, i.e. finding it from the Anderson impurity problem.

Impose self-consistency for the bath: full dynamical mean field theory is recovered.
Excitations in Mott Insulators

Classical systems: MnO ($d_5$), FeO ($d_6$), CoO ($d_7$), NiO($d_8$); parent materials for HTSCs: CaCuO$_2$, La$_2$CuO$_4$ ($d_9$). Neel temperatures 100-500K. Energy gaps 20,000+ K. Remain insulating both below and above $T_N$.

**LDA/ LDA+U**, other static mean field theories, cannot access paramagnetic insulating state.

Cannot explain the existence of Zhang-Rice states.

Cannot explain waterfalls, disappearance of spectral weight and so on.
LDA+DMFT for HTSCs: Dispersion of Zhang-Rice singlet

Single-site DMFT

Two-site Cluster ED

\[ \Sigma(k, \omega) = \Sigma_{11}(\omega) + \Sigma_{12}(\omega)[\cos(k_x) + \cos(k_y)] \]

\[ \Sigma_{11}(\omega) \]

\[ \Sigma_{12} \]

\[ \Sigma_{22} \]

\[ \omega \]

\[ \Sigma \]

\[ e \]

\[ \text{Sr}_2\text{CuO}_2\text{Cl}_2 \]

\[ \text{Energy (eV)} \]

\[ \text{Yin, Gordienko, Wan, SS, PRL 2008} \]
Waterfalls in HTSCs: Main Features

Features of recent ARPES data:

• Doping-independent Fermi velocities

• Disappearance of spectral weight at Gamma

• Existence of two energy scales

FIG. 2. Intensity plot of data shown in Fig. 1 as functions of the binding energy and momentum. The data was symmetrized around the $\Gamma$ point. Also shown on the plot are the dispersions obtained by following the peak positions of the MDCs (solid line) and the EDCs (circles and triangles). The results are compared with the shifted dispersion from the LDA calculation (dashed line).

Ronning et.al PRB 2005
Assume two-pole approximation:

\[ \Sigma(\omega) = \frac{W_1}{\omega - P_1} + \frac{W_2}{\omega - P_2} \]

One-electron Green Function:

\[ G(k, \omega) = \begin{pmatrix} \omega - \epsilon_d - \Sigma(\omega) & -V_{pd}(k) & -V_{pd}(k) \\ -V_{pd}(k) & \omega - \epsilon_p & 0 \\ -V_{pd}(k) & 0 & \omega - \epsilon_p \end{pmatrix}^{-1} \]

Spectrum of Excitations from effective 5x5 Hamiltonian:

\[ H_{aux} = \begin{pmatrix} \epsilon_d & V_{pd}(k) & V_{pd}(k) & \sqrt{W_1} & \sqrt{W_2} \\ V_{pd}(k) & \epsilon_p & 0 & 0 & 0 \\ V_{pd}(k) & 0 & \epsilon_p & 0 & 0 \\ \sqrt{W_1} & 0 & 0 & P_1 & 0 \\ \sqrt{W_2} & 0 & 0 & 0 & P_2 \end{pmatrix} \]

k-dependent hybridization

\[ V_{pd}(k) = \sum_R e^{ikR}V_{pd}(R) = 2t[\sin(k_xa) + \sin(k_ya)] \]

disappears at \( \Gamma \) point

\[ V_{pd}(k = 0) = 0 \]
Waterfalls in HTSCs: Oxygen Content in ZR singlet

**C-DMFT** calculations with three pole approximated self-energies:

- **Blue fat lines** show the amount of oxygen in the ZR band
- **Numbers** show actual number of electrons in the ZR band

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![Graph of La$_2$CuO$_4$]

Yin, Gordienko, Wan, SS, PRL 2008
Generalized Zhang-Rice Physics

$\text{CuO}_2(d^9)$

$SO=1/2$  $SCu=1/2$

Zhang-Rice Singlet ($S_{tot}=0$)

$\text{NiO}(d^8)$

$SO=1/2$  $SNi=1$

Doublet ($S_{tot}=1/2$)

$\text{CoO}(d^7)$

$SO=1/2$  $SCo=3/2$

Triplet ($S_{tot}=1$)

$\text{FeO}(d^6)$

$SO=1/2$  $SFe=2$

Quartet ($S_{tot}=3/2$)

$\text{MnO}(d^5)$

$SO=1/2$  $SMn=5/2$

Quintet ($S_{tot}=2$)
NiO: LDA+DMFT compared with ARPES

Dispersion of doublet


Paramagnetic state of NiO: The blue linewidth and the numbers show the oxygen content and the amount of electrons in the ZR band.
CoO: LDA+DMFT compared with ARPES

Dispersion of triplet

Paramagnetic state of CoO: The blue linewidth and the numbers show the oxygen content and the amount of electrons in the ZR band.

Atomic Multiplets in Photoemission of Americium

Atomic multiplet structure emerges from measured photoemission spectra in Am (5f⁶), Sm (4f⁶) -

Signature for f electrons localization.

**Am Equation of State: DMFT Predictions**

DMFT predictions are much better than DFT-LDA:
- Non magnetic $f^6$ ground state with $J=0$ ($^7F_0$)
- Equilibrium Volume:
  $$V_{\text{theory}}/V_{\text{exp}} = 0.93$$
- Bulk Modulus: $B_{\text{theory}}=47$ GPa
  Experimentally $B=40-45$ GPa

Accounting for full atomic multiplet structure using Slater integrals:
$$F^{(0)}=4.5 \text{ eV}, F^{(2)}=8 \text{ eV}, F^{(4)}=5.4 \text{ eV}, F^{(6)}=4 \text{ eV}$$

**Theoretical P(V) using DMFT**

Predictions for Am I

Predictions for Am II

Predictions for Am III

Predictions for Am IV
Many Body Electronic Structure for $\gamma$F$^0$ Americium

Experimental Photoemission Spectrum after J. Naegele et.al, PRL 1984
Calculated Electronic Structure using DMFT

**UO$_2$**

XPS & BIS data after Veal and Lam, Solid State Communications 33, 885 (1980)

**PuO$_2$**

Calculating Kondo Exchange Energy

Minimal Hamiltonian for heavy fermion superconductors – Kondo lattice

\[ H = - \sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + J_K \sum_i S_i \left( \sum c_{i\sigma}^+ \tau_{\sigma\sigma'} c_{i\sigma'} \right) \]

Solutions can be obtained accurately using Continuous Time Quantum Monte Carlo Method and Dynamical Mean Field Theory

Ce-122 and Ce-115 compounds
Antiferromagnetism competes with superconductivity (Tc’s~1-4K).
Specific heat values range from 250 to 750 mJ/mol*K².

PuCoGa₅ has superconducting Tc~18.5K

Needs for Material Specific Input from LDA+DMFT calculation.
Describing Kondo systems with LDA+DMFT

Framework of the realistic simulation

For given materials, e.g. $\text{CeX}_2\text{Si}_2$ $X=$Rh,Pd,Au,Ag,Cu,Ru

LDA+DMFT (Hubbard I)

Hybridization function $\Delta(\epsilon) = \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$

Schrieffer-Wolff transformation $\rightarrow$ Kondo coupling $J_K$

+ crystal-field, spin-orbit splittings

Realistic Kondo (Coqblin-Schrieffer) lattice model

DMFT with CT-QMC as the impurity solver

First-principle result for heavy fermions!
Kondo Coupling Strength Ce 122 Compounds

CeD$_2$Si$_2$ where
D=Mn,Fe,Co,Ni,Cu – 3d
D=Ru,Rh,Pd,Ag – 4d
D=Os,Au – 5d

Most widely studied, in particular due to discovery of heavy fermion superconductivity in CeCu$_2$Si$_2$

Ag,Au,Pd - 10K AFM, Rh – 40K AFM
Cu,Co,Fe,Ni,Ru,Os - PM
Mn – 379K AFM due to Mn moments
Calculated Hybridization for Ce 122 Compounds

Inputs to CT-QMC calculated by LDA for $\text{CeX}_2\text{Si}_2$

$$\Delta(\epsilon) = \sum_k V_k^2 \delta(\epsilon - \epsilon_k)$$

Schrieffer-Wolff transformation

$$J_K = \frac{1}{\pi} \frac{\text{Tr} \int_{-D}^D d\epsilon \text{Im}\Delta(\epsilon)}{N_d} \left( \frac{1}{|\epsilon_f|} + \frac{1}{\epsilon_f + U} \right)$$

$$\epsilon_f = -2.5[\text{eV}], \quad U = 5[\text{eV}], \quad D = 5[\text{eV}]$$

“conduction-band” Green’s function

$$G_c(i\omega_n) = \frac{1}{\pi} \frac{1}{N_d} \int_{-D}^D d\epsilon \frac{\text{Tr}\text{Im}\Delta(\epsilon)}{i\omega_n - \epsilon} \frac{1}{\int_{-D}^D d\epsilon \text{Tr}\text{Im}\Delta(\epsilon) / \pi N_d}$$
Tracking a magnetic phase transition of CeRh$_2$Si$_2$

Néel temperature $T_N = 41$[K]
Material-specific Doniach phase diagram

Artificially rescale the Kondo coupling (qualitatively imitating the pressure experiments)

CeRh$_2$Si$_2$ is closer to the quantum critical point than CePd$_2$Si$_2$
Summarizing the material-specific Doniach phase diagrams

heavy fermion materials are close to the quantum critical point
The materials align like from the right to the left:
(quantum critical point) > CeRh$_2$Si$_2$ > CePd$_2$Si$_2$ ~ CeAu$_2$Si$_2$ > CeAg$_2$Si$_2$ > CeAs
Restoring the universal Doniach phase diagram

Hund coupling effects in $f^2$ states give us a factor of ~30% in the Kondo coupling

taken as the point where the Neel temperature vanishes
Calculations of RKKY Interactions

\[ \mathcal{H} = -\sum J_{ij} S_i \cdot S_j \]

2d order perturbation theory for Kondo impurity hamiltonian

\[ H = -\sum_{ij\sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + J_K \sum_i S_i \left( \sum_{\sigma} c_{i\sigma}^+ \tau_{\sigma\sigma} c_{i\sigma} \right) \]

produces the scaling \( J_{RKKY} \approx J_K^2 N(0) \)

More general expression for exchange constants is obtained using magnetic force theorem: (Lichtenstein et. al 1987)

\[ J_{\alpha\beta}^{\tau_R R'_{\tau'}} = \sum_{\mathbf{q}} \sum_{k,j,j'} \frac{f_{k,j} - f_{k+\mathbf{q},j'}}{\epsilon_{k,j} - \epsilon_{k+\mathbf{q},j'}} \langle \psi_{k,j} | [\sigma \times \mathbf{B}_{\tau}]_{\alpha} | \psi_{k+\mathbf{q},j'} \rangle \]

\[ \langle \psi_{k+\mathbf{q},j'} | [\sigma \times \mathbf{B}_{\tau'}]_{\beta} | \psi_{k,j} \rangle e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}')} \] (2)

Important to understand interplay between Kondo and RKKY interactions for heavy fermion systems using realistic electronic structures.
Material design: Once Kondo exchange $J_K$ and local moment interaction ($J_{RKKY}$) are computed one can apply pressure or doping.

Searching for magnetism in Plutonium:
* Pu is non magnetic: $f^5 + Kondo$? (Shim, Nature 2007), $f^6$ (Shick, PRB 2006)
* Mixing with Am expands the lattice up to 20%, can Pu moment be seen?
$J_K > J_{RKKY}$ for $0.0 \leq x \leq 0.5$

- No moment due to Kondo screening
- No quantum criticality and superconductivity

(MJ. Han, X. Wan, SS, PRB 2008
Combination of **electronic structure** and **many body** dynamical mean field methods open new avenues in studying strongly correlated systems:

- It allows to simulate structural phases, equations of states, volume expansions and collapses.
- It allows to resolve Kondo resonances, atomic multiplet spectra and mixed valence regimes.
- It allows to study Doniach phase diagrams and quantum critical behavior.
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